UNIVERSITY OF BIRMINGHAM

Production of 5-Hydroxymethylfurfural in Novel Deep Eutectic Solvents

By

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Abstract

The conversion of lignocellulosic biomass to biofuel or its precursors has recently received the attention of many researchers because of their use as potential sources of transportation fuels, and for being both non-toxic and biodegradable. 5-Hydroxymethylfurfural (5HMF) has been discovered to be a precursor for biofuel production and can be produced from biomass, which is readily available, renewable, and sustainable. Consequently, 5HMF is used to produce Dimethylfuran (DMF), which is a biofuel with characteristics similar to petrol and other high-value chemicals. A commercialised 5HMF production has been impeded by the lack of an efficient, greener, and low-cost process which does not require the simultaneous use of catalyst and solvent. In this study, a novel self-catalysed Deep Eutectic Solvent (DES) was formulated, modified, and tested for the dehydration of fructose to 5HMF. The process was optimised in terms of 5HMF yields and fructose conversion for the following reaction factors: temperature, time, formulated DES salt-to-acid ratio and feed ratio (fructose-to-DES). The reaction kinetics were also investigated, while the effect of the novel DES composition on the dehydration reaction was explored.

The DESs were prepared using a Brønsted acid (p-toluenesulfonic acid (p-TSA)) and a dicarboxylic acid (adipic acid) and organic salts such as choline chloride (ChCl) and diethylethanolammonium chloride (DEAC). The acids perform a dual role as both a hydrogen bond donor (HBD) for the DES composition and a catalyst for the dehydration reaction. The different reaction parameters were investigated and optimised in a batch system featuring reaction temperature (50 – 110 °C), reaction time (5 – 180 min), feed ratio (fructose mass to DES mass) (2.5 – 100 g/g) and DES molar mixing ratio 0.5:1 to 2:1 (salt-to-acid). The first DES system was composed of ChCl

and p-TSA, where it was found that fructose was readily dehydrated to 5HMF. The acquired results showed that the highest 5HMF yield of 78.3% was obtained at a temperature of 80 °C and reaction time of 60 min, using a DES molar mixing ratio of 1.5:1 (ChCl-to-p-TSA) and a feed ratio (initial fructose concentration) of 5.

To investigate the effect of changing the DES composition, a different organic salt was used. The second DES system was composed of the inexpensive N,N-diethylethanolammonium chloride (DEAC) as an organic salt and p-TSA as an HBD. The advantage of using this DES is its ability to act as a solvent and catalyst simultaneously. It was shown to actively catalyse the dehydration reaction of fructose under moderate reaction conditions with a high 5HMF yield of 84.8% obtained at a reaction temperature of 80 °C, a reaction time of 60 min, a DES molar mixing ratio of 0.5:1 DEAC-to-p-TSA, and feed ratio (initial fructose ratio) of 5.

For the third DES, a new acid was used to study the influence of changing the DES composition. The third DES was composed of adipic acid, which is a weak dicarboxylic acid, as the HBD and ChCl as the organic salt. The dehydration reaction was carried out in an open system at mild reaction conditions. One hundred percent fructose conversion was achieved, giving a 5HMF yield and selectivity of 90.8% at a reaction temperature of 90 °C and at a reaction time of 120 min, using a DES molar mixing ratio of 1:1 (salt-to-acid) and feed ratio (initial fructose) of 2.5.

The kinetics of the reactions were studied and showed close to 1 order for DES1 and DES2 and close to 1.8 order for DES3. An increase in the rate of reaction with temperature was observed for the three DES systems that were formulated and investigated.

Dedication

To my Mum

(1955–2014)

I still remember that day when I left to start my PhD; you hugged me and whispered in my ear, “I am waiting to hug you when you return with your PhD”.

Now I am close to achieving what I promised you that day. Unfortunately, you won’t be there to hug me again. However, I am confident that you can see what I am writing to you: Mum, I kept my promise and soon will be getting my PhD, which I dedicate fully to you. May Allah rest your soul in peace and heaven.

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I want to thank my family for their important role in enabling me to complete this programme. My gratitude also goes to Mrs H Abulgassem for her unlimited and logistical support, and kind advice throughout the whole period of study.

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Table of Abbreviations

([HO_2CMMIm]Cl)	1-Carboxymethyl-3-methylimidazolium chloride
[4.2H] [HSO^-_4]$_2$	Unsymmetrical dicationic ionic liquid [tetraEG (mim)(triethylamo)]
[BeMIm]Cl	1-Benzyl-3-methylimidazolium chloride
[BMIM]BF_4	1-Butyl 3-methyl imidazolium tetrafluoroborate
[BMIM]Cl	1-Butyl-3-methyl imidazolium chloride
[C_4mim]Cl	1-Butyl-3-methylimidazolium chloride
[CMIM]Cl	1-Carboxypropyl-3-methyl imidazolium chloride
[Emim]Br	1-Ethyl-3-methyl-imidazolium-bromide
[Emim]Cl	1-Ethyl-3-methylimidazolium chloride
[HMIm]Cl	1-H-3-methyl imidazolium chloride
[MIMPS]$_3PW_{12}O_{40}$	1-(3-sulfonicacid) propyl-3-methyl imidazolium phosphotungstate
[OMIM]Cl	1-Methyl-3-octylimidazolium chloride
[TetraEG (mim)$_2$][OMs]$_2$	Room temperature ionic liquid
2-PrOH	2- Propanol
5HMF	5-Hydroxymethylfurfural
AC	Active carbon
$Ag_3PW_{12}O_{40}$	Heteropolyacid salt (lab. Prepared sold catalyst)
$H_3PW_{12}O_{40}$	Lab. Prepared solid catalyst consisting of phosphotungstic acid
BHC	Betaine hydrochloride
ChCl	Choline chloride
COOH	Carboxyl functional group

$Cu(NTf)_2$	Copper(II) triflate
DAD	Diode array detector
DEAC	N,N-diethylethanolammonium chloride
DES	Deep eutectic solvent
DMA	N,N-dimethylacetamide
DMAC	Dimethylacetamide
DMF	N,N-Dimethylformamide
DMF	Dimethylfuran
DMSO	Dimethyl sulfoxide
DOE	US Department of Energy
DOE	Design of experiment
GC MS	Gas chromatography mass spectrometry
GLc NH_4	D-glucose amine
HBD	Hydrogen bond donors
HPAs	Acid–base bifunctional heteropolyacids (Ly_2HPW)
HPLC	High pressure liquid chromatography
IL	Ionic liquids
LCC	Lignin acid solid catalyst
MBDOE	Million barrels per day of oil equivalent
MIBK	Methyl isobutyl ketone
MIL-101(Cr)-SO_3H	Sulfonic acid-functionalised metal–organic
M-ZrPO-0.75	Mesoporous zirconium oxophosphate with P/Zr molar ratio of 0.75
NMR	Nuclear magnetic resonance

nRIU	Nano Refractive Index Unit
OFAT	One factor at a time
p-TSA	p-Toluenesulfonic acid
pTsOH	p-Toluenesulfonic acid
PyHCl	Pyridine hydrochloride
RPM	Round per minute
$Sc(OTf)_3$	Scandium trifluoromethanesulfonate
$R\text{-}SO_3H$	Sulphonic acid
SO_3 OH	Functionalised acidic ionic liquid with hydrogen sulphate anion
SO_4^{2-} /ZrO_2-Al_2O_3	Commercial solid catalyst
TBAB	Tetra n-butyl ammonium bromide
TBAC	Tetra n-butyl ammonium chloride
THF	Tetrahydrofuran
TiSBA-15	Mesoporous solid catalyst
VWD	Variable wavelength detector

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction

1.1 Background

Securing energy resources, keeping the environment safe from pollutants and economic growth are core factors for any country's energy policy. The global consumption of energy is increasing in parallel with the world population growth, as illustrated in Figure 1.1. The global population was estimated to be more than 7 billion in 2014. This expansion in world population has led to a rapid increase in fossil resources depletion, and energy consumption is expected to increase by 30% over the coming two decades (Kobayashi et al., 2012). To cope with this increase in consumption and population, reliable energy resources have to be in place.

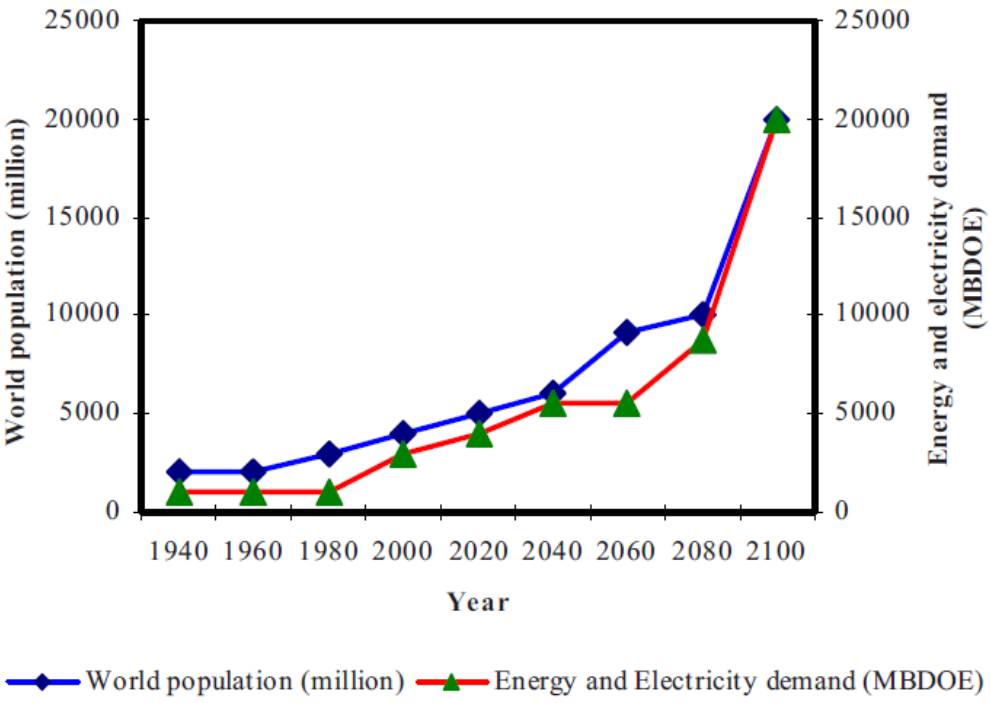


Figure 1.1. The estimation of increasing energy demand vs world population from 1940 to 2100 (Omer, 2009)

A previous study by the World Energy Council revealed that the world demand for energy in 2020 would be 50 to 80% higher compared with the levels in 1990. Global energy consumption is estimated to increase from 2×10^9 kW h per year in 2009 to 53×10^9 kW h per year by 2020 (Omer, 2009). In India alone, up to the 31st of March 2013, the annual energy consumption from oil, natural gas and coal (thermal) was 151.3 GW, 4.80 GW from nuclear energy, 30.50 GW from hydro and 27.54 GW from renewable energy (Kumar et al., 2015), as illustrated in Figure 1.2. The energy consumption of fossil fuels in India increased from 64% in 2004 (Pillai and Banerjee, 2009) to 68% in 2013.

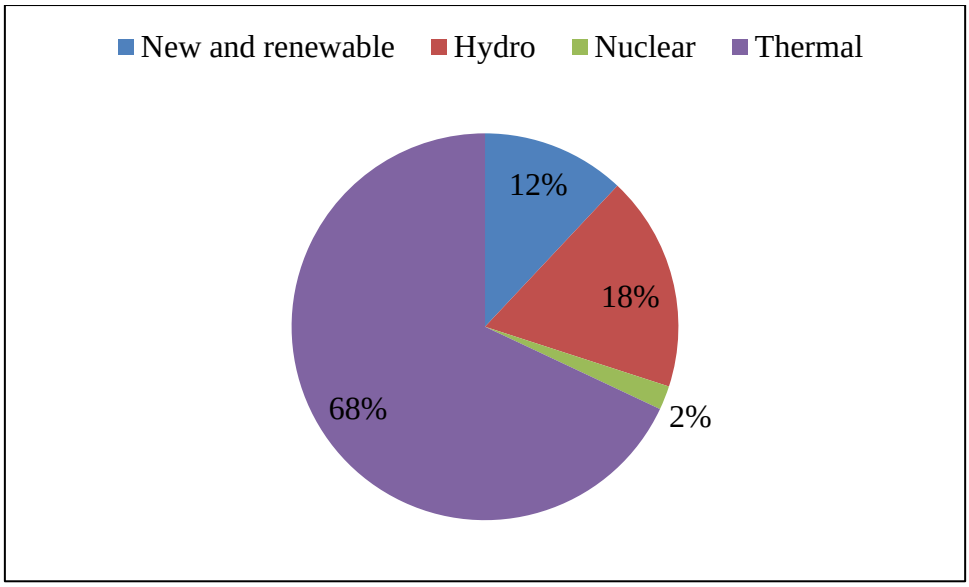


Figure 1.2. The contribution of different energy resources in India up to 31st of March 2013 (Kumar et al., 2015)

Meanwhile, in the United States, the total consumption of energy was 1.02×10^{24} Joules in 2011. Eighty-two percent of this consumed energy was obtained from fossil resources (Juneja et al., 2013). The transportation sector itself accounted for one-third of the total energy consumed worldwide, giving rise to 21% of the global greenhouse gas (GHG) emissions (Banowetz et al., 2008). These statistics clearly demonstrate the

dependency of the world on fossil fuel resources as the dominant energy source. Fossil fuel resources are non-renewable and the main source for unwanted emissions, which could be a direct reason for the global warming phenomenon (Schaub and Vetter, 2008). However, the unsustainability of fossil fuels in terms of unstable prices, limited or non-renewable resources, the ecological effect and the resultant increase in greenhouse gas emissions have influenced researchers to seek environmentally friendly and more reliable alternative energy resources (Ni and Sun, 2009, Schaub and Vetter, 2008, Despax et al., 2013). Among the wide diversity of renewable energy resources, lignocellulosic biomass, in particular, has been recognised as a sustainable source (Stöcker, 2008).

1.2 Lignocellulosic Biomass

Lignocellulosic biomass consists of non-edible components such as the wastes of trees, harvest, the timber industry, food, and animals. Lignocellulosic biomass is the foundation of second-generation biofuels; it replaces the first-generation biofuels feedstock, which directly threatened the security of human food resources. It is estimated that in the United States of America alone, the annual production of dry biomass from forest waste and agriculture is approximately 1.3 billion tons (Bond et al., 2010). Second generation biofuels feedstock is mainly derived from lignocellulose, which is the foremost component in the composition of plants and algae. Lignocellulose is composed of three main parts, namely lignin, cellulose and hemicellulose. In addition, it contains minor amounts of other materials such as protein and pectin. The proportion of the three parts depends on the plant or the source, but normally the percentages of the portions are 40 to 50 wt% of cellulose, 20 to 40 wt% of hemicellulose and 18 to 35 wt% of lignin, as shown in Figure 1.3.

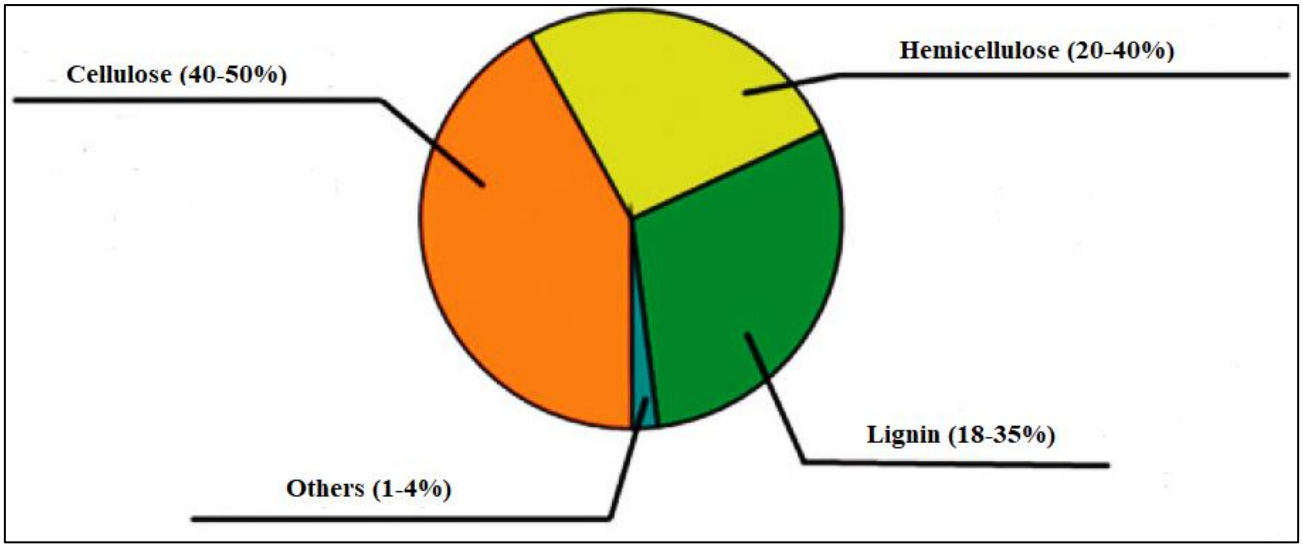


Figure 1.3. The composition of lignocellulose biomass of wood (Sun et al., 2011)

This interest in lignocellulosic biomass has been driven by different factors. Firstly, it can efficiently reduce the dependency on fossil fuels as it is widely spread. This may lead to a reduction in poverty and an increase in employment in rural areas. Secondly, it can be easily converted to green energy (Bilgili and Ozturk, 2015). Thirdly, it does not deplete human food resources. Biomass is composed of lignin, fatty acids, lipids, carbohydrates, and many other components. A total of 170 billion tons of biomass are produced from nature by photosynthesis annually. Approximately 75% of this huge amount of biomass is carbohydrates (Caratzoulas and Vlachos, 2011). It is worth mentioning that carbohydrates, particularly the ones obtained from lignocellulosic biomass, are known as the largest natural source of carbon, despite the profusion of oxygen in their structure. They produce useful chemicals such as furans and levulinic acid (Van Putten et al., 2013). The US Department of Energy (DOE) reported that furans, considered as one of the top ten chemicals, have the potential to produce biofuels and many other useful products (Abdulmalik et al., 2005). 5-Hydroxymethylfurfural (5HMF)

is one of the main chemicals mentioned that has the ability to produce useful biopolymers, chemicals and fuels.

1.3 5-Hydroxymethylfurfural as a Block Intermediate Chemical

5HMF is a heterocyclic furan compound consisting of two functional groups, aldehyde and hydroxide. As shown in Figure 1.4, 5HMF is produced from biomass resources through a variety of carbohydrates and it has useful downstream derivatives in the form of chemicals and biofuels. Some of its physical and chemical properties are listed in Table 1.1. 5HMF is found to be safe and has a negligible toxicological effect on humans; it was detected as a product of the thermal decomposition of carbohydrates in the human diet (Van Putten et al., 2013).

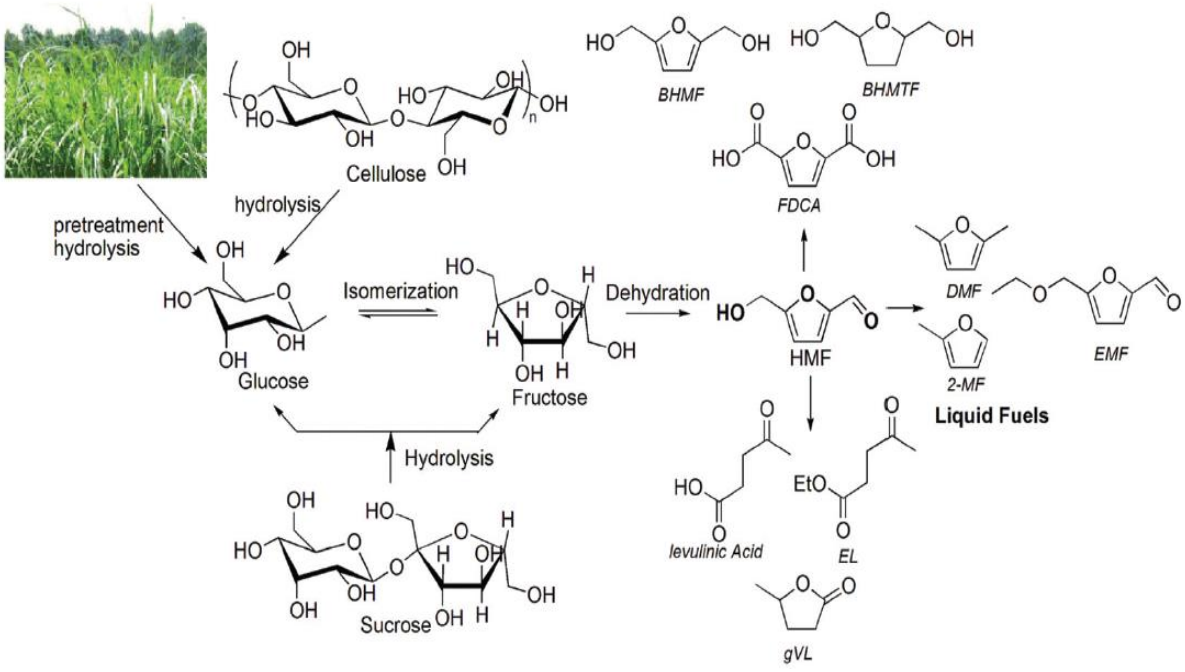


Figure 1.4. Production of 5HMF from biomass resources and its downstream products (Saha and Abu-Omar, 2014)

Table 1.1. Physical and chemical properties of 5HMF (Van Putten et al., 2013)

Property	Value
CAS Registry number	67-47-0
Chemical Abstracts name	5-(hydroxymethyl)-2-furancarboxaldehyde
Synonyms	5-(hydroxymethyl)-2-furaldehyde, HMF, 5-(hydroxymethyl)-2-furancarbonal, 5-(hydroxymethyl)-2-furfural, 5-hydroxymethyl-2-formylfuran, 5-oxymethylfurfurole, hydroxymethyl furfuraldehyde
Molecular formula	$C_6H_6O_3$
Molecular weight (g/mol)	126.11
Colour	Yellow powder
Odour	Chamomile flowers
Boiling point °C	114 – 116
Melting point °C	28 – 34
Solubility	Freely soluble in water, methanol, ethanol, acetone, ethyl acetate and dimethylformamide
Toxicity	Acute toxicity (LD50 Oral - Rat - 2,500 mg/kg)
Density g/cm^3	1.243 at 25 °C
Flash point °C	79
UV absorption nm	283
Refractive index	1.5627 at 18 °C

5HMF was discovered over 100 years ago as a product of hexose dehydration. The first reported synthesis of 5HMF was in the late 19th century by Dull and Kiermayer (Van Putten et al., 2013). It was described by the DOE as one of the top ten added-value chemicals, which can be used to produce many useful chemicals and fuels (Bozell and Petersen, 2010).

Synthesis of 5HMF comes from the dehydration of C6 carbohydrates, including polymeric and monomeric carbohydrates such as cellulose, inulin, starch, sucrose, glucose

and fructose. 5HMF plays the role of bridging the gap between the resources of biomass and the wide range of useful biochemical products, as illustrated in Figure 1.5 (Teong et al., 2014). In addition to 5HMF being naturally obtained by the catalytic thermal processing of different hydrocarbons, it can also be found in many types of processed food and food resources (Martins and Van Boekel, 2005).

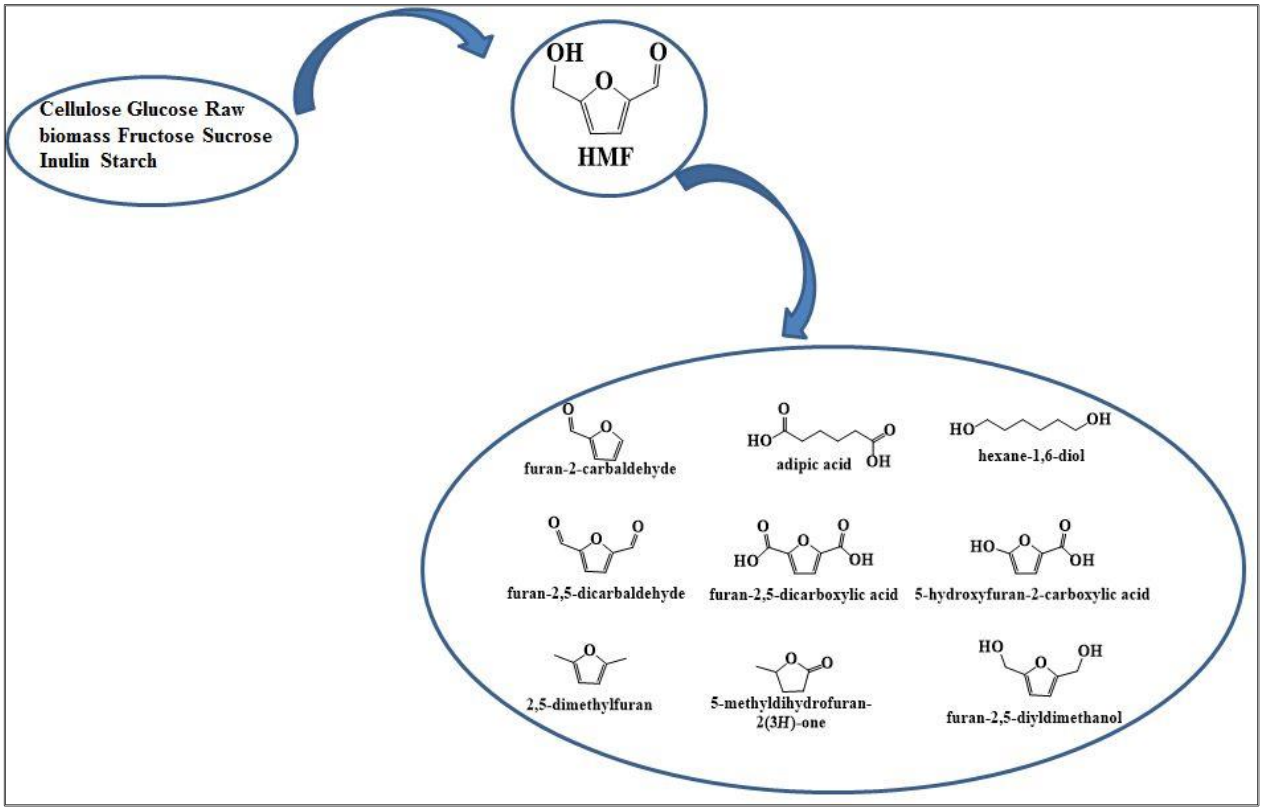


Figure 1.5. 5HMF bridging the gap between biomass resources and useful products of chemicals and fuels (Teong et al., 2014)

1.4 Why 5HMF is Being Produced

There has been growing interest in 5HMF since the late 19th century. Although 5HMF itself has a relatively high boiling point, which has led to a shrinking in its market, a greater interest has been paid to its downstream products as it is a very useful and important block intermediate material in the production of added-value chemicals and

pharmaceutical products (Ma et al., 2011). 5HMF can be processed, for example, to produce levulinic acid and furan derivatives as potential sources of bioplastics, other useful chemicals (Cukalovic and Stevens, 2010) and biofuels (Zakrzewska et al., 2011). Figure 1.6 illustrates the most important added-value chemicals and fuels which can be produced by different processes from 5HMF.

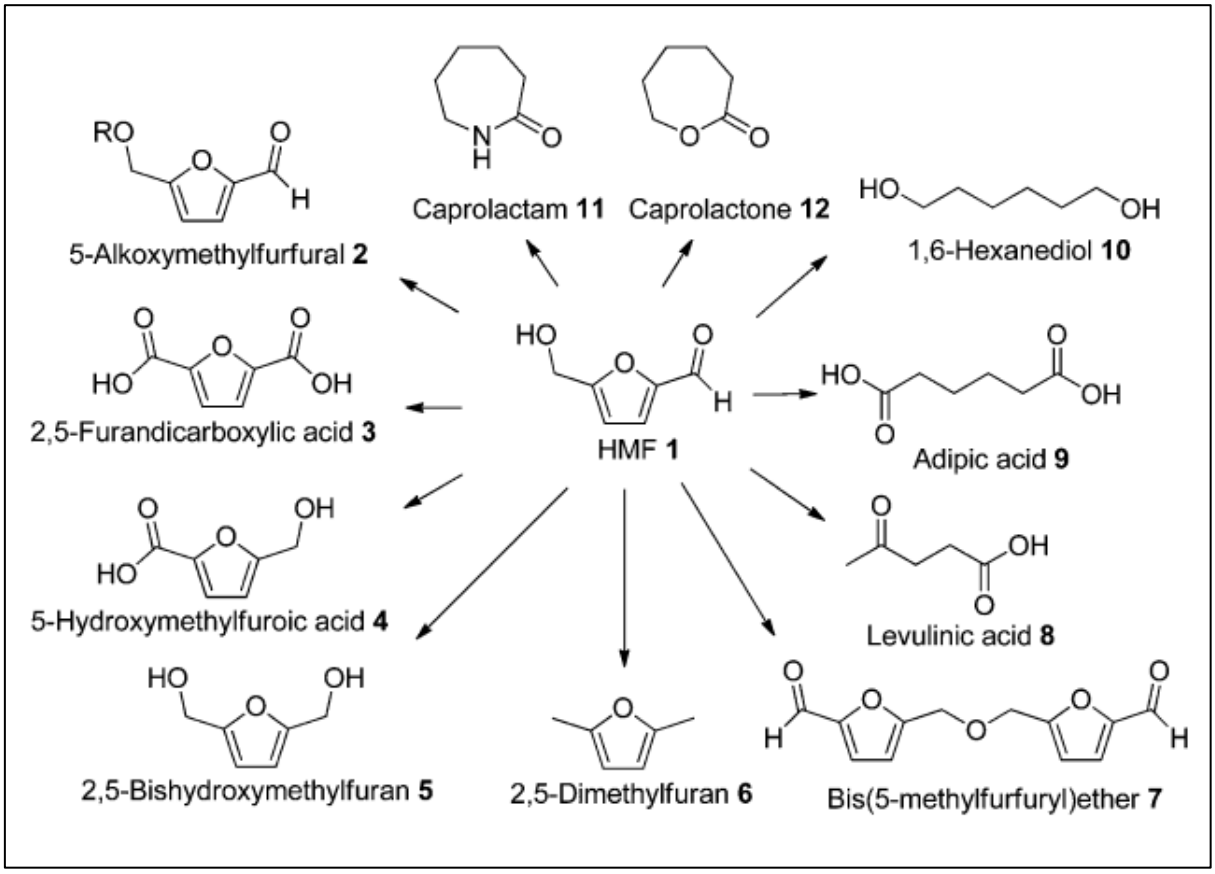


Figure 1.6. 5HMF derivatives (Van Putten et al., 2013)

The 5HMF derivatives illustrated in Figure 1.6 above are classified in furan and non-furan components, and some of their applications are highlighted in Table 1.2.

Table 1.2. Classification of 5HMF derivatives and their applications (Van Putten et al., 2013)

Furanic 5HMF derivatives		
No.	Compound Name	Applications
2	5-Alkoxymethylfurfural	Fuel additives
3	2,5-Furandicarboxylic acid	Block intermediate to produce polyesters
5	2,5-Bishydroxymethylfuran	Pharmaceutical, polymers and resin additives
6	2,5-Dimethylfuran	Bio petrol
7	Bis(5-Methylfurfuryl)ether	Fuel additives
Non-furanic 5HMF derivatives		
No.	Compound Name	Applications
8	Levulinic acid	Polymers, reagents, photography, batteries
9	Adipic acid	Pharmaceutical, bioplastics and reagent
10	1,6-Hexanediol	Polyesters, dyes and adhesives
11	Caprolactam	Nylon industry
12	Caprolactone	Polymers

1.4.1 The Historical Background of 5HMF Synthesis from Biomass Development

The synthesis of 5HMF was first reported by Dull at the end of the 19th century, when he heated inulin in the presence of a pressurised oxalic acid solution (Rosatella et al., 2011). Over time, interest has been growing in developing a variety of systems to produce 5HMF from biomass resources. Historically, the development of 5HMF synthesis can be summarised in three main periods, as illustrated in Figure 1.7: firstly, the starting period

from the late 19th century to 1980; secondly, the growth–development period from 1980 to 2000; and thirdly, the most active period from 2000 onwards.

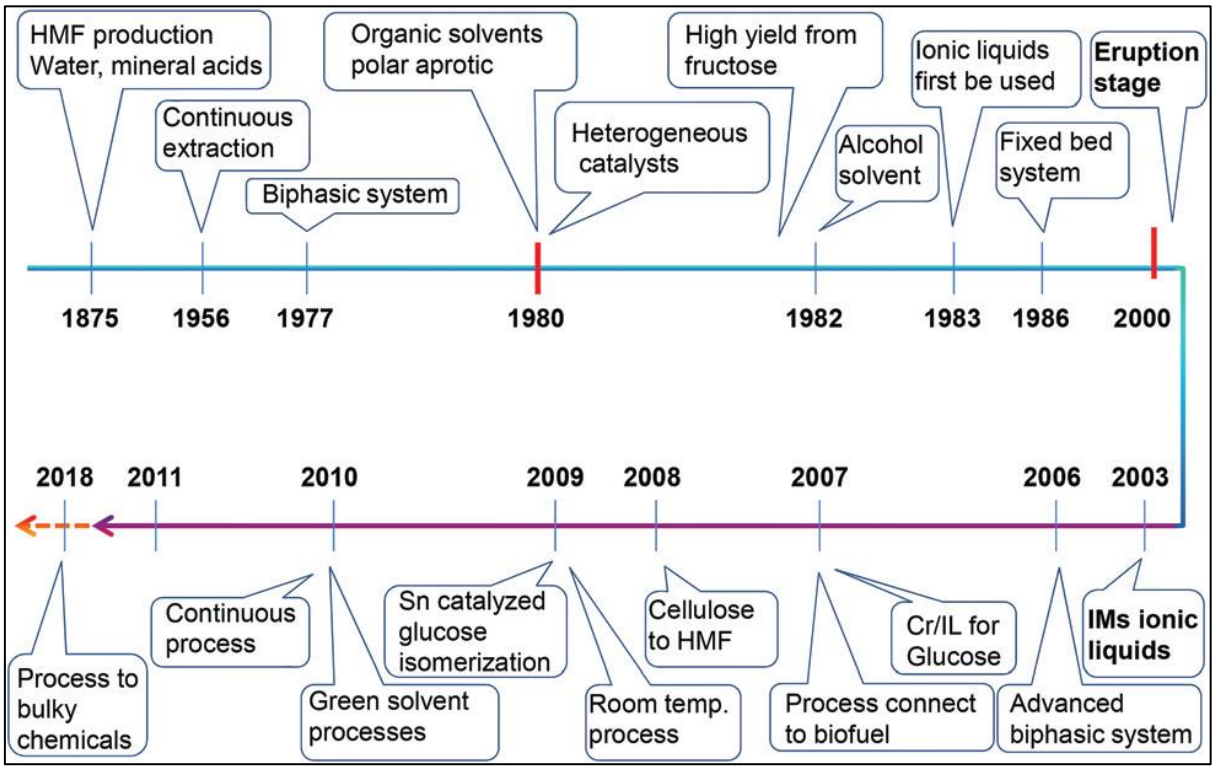


Figure 1.7. The historical development of 5HMF synthesis from biomass (Teong et al., 2014)

1.4.2 The Starting Period from the late 19th Century to 1980

In this period of time, the synthesis of 5HMF started slowly at the end the 19th century. The first review publication in this field was in 1951 by (Newth, 1951). The research work was mainly focused on investigating the capability of mineral acid catalysed aqueous systems on the dehydration of carbohydrates to 5HMF, where water was the prevalent solvent used for the dehydration process (Moye, 1964). A variety of biomasses such as corn starch, glucose (Mednick, 1962), wood chips, and fructose (Kuster, 1977) were examined using mineral organic acid catalysis and non-catalysis media. The

development of the aqueous system was restricted by several factors, such as the requirement for severe reaction conditions (time, temperature, and pressure) to achieve high selectivity of 5HMF. The presence of water as a solvent in the dehydration reaction caused 5HMF rehydration to levulinic acid and formic acid (Van Putten et al., 2013). Furthermore, 5HMF polymerisation or cross-polymerisation with carbohydrates produces humins, which lead to a reduction in 5HMF yield. To overcome these drawbacks of the aqueous system and increase the selectivity towards 5HMF, a continuous extraction system consisting of n-butanol as the organic phase was invented by Pineston in 1956 (Teong et al., 2014). This finding led to an increase in the 5HMF yield in a shorter reaction time as a result of suppressing the side reactions by continuously removing the 5HMF produced from the aqueous system to the organic system (Kuster and van der Steen, 1977). This invention has paved the way for a new technique, namely a biphasic system, which combines the aqueous system with organic solvents for continuous extraction.

1.4.3 The Growth–Development Period from 1980 to 2000

During this period of time, interest grew in investigating fructose dehydration to 5HMF using heterogeneous (Musau and Munavu, 1987) and homogeneous (Antal et al., 1990) catalysts, simultaneously with increasing interest in developing biphasic systems and studying the viability of involving organic solvents in the dehydration of a variety of carbohydrates to 5HMF. Different organic solvents were studied in catalytic and non-catalytic systems. DMSO was the first active organic solvent reported in sugars' dehydration to 5HMF in 1980. It has the ability to dissolve most sugars and is capable of stabilising 5HMF (Nakamura and Morikawa, 1980). The development of organic solvents was limited by several factors, including that they are not environmentally friendly, are expensive and have high boiling points. In addition, there is the difficulty of product

separation and energy consumption (Kuster, 1990). Dehydration of fructose in different alcohol solvents such as n-butanol, methanol, ethanol and iso-propanol was reported (Brown et al., 1982). Despite the lower boiling point of these solvents compared to DMSO, the yields of 5HMF obtained were still not promising.

1.4.4 The Most Active Period from 2000 Onwards

By the beginning of the 21st century, the worldwide energy demand had increased tremendously. This came as a result of the increasing growth in world population, depletion and fluctuation in oil prices and the political instability in production zones. All of these factors and more have led to a greater interest in developing the manufacturing of 5HMF from carbohydrates as an intermediate in the production of sustainable sources of energy (Van Putten et al., 2013). Since 2000, a number of new systems and old systems for carbohydrate dehydration have been developed (Teong et al., 2014), such as the dehydration of different carbohydrates in aqueous systems with no use of catalysts (Watanabe et al., 2005, Wu et al., 2010, Aida et al., 2007). Fructose dehydration to 5HMF was also studied using different catalytic systems such as phosphates (Benvenuti et al., 2000), metal oxides (Chareonlimkun et al., 2010), metal halides (Davis et al., 2011) and organic acids (Li et al., 2009). Later, the fructose dehydration to 5HMF in aqueous systems was studied using different solid acids as catalysts (Jadhav et al., 2013). Despite the fact that water is a green solvent and sugars have high solubility in water, aqueous systems produce low yields of 5HMF. This low yield is attributed to the characteristics of 5HMF as a compound with high solubility and low stability in water.

Different polar organic solvents such as DMSO, DMA, and DMF were studied in the dehydration of carbohydrates to 5HMF using a variety of heterogeneous and homogeneous catalysts. A remarkable yield of 5HMF (95.2%) obtained from fructose dehydration in

DMSO was achieved, while 90% 5HMF yield achieved when the DMA and DMF were used (Seri et al., 2000). Despite the high 5HMF yield obtained by using elevated-boiling-point organic solvents, scaling up the process was not feasible due to the product separation difficulties. To overcome this, interest grew in using low-boiling-point organic solvents in carbohydrates' dehydration to 5HMF (Ohara et al., 2010). Dumesic's group has recently studied new kinds of solvents obtained from biomass, namely γ-valerolactone (GVL) and γ-hexalactone (GHL) in the carbohydrates' dehydration to 5HMF (Gallo et al., 2013). The same group has recently studied the biphasic system intensively; most of the conducted studies focused on the continuous extraction of 5HMF from water (Roman-Leshkov et al., 2006, Roman-Leshkov and Dumesic, 2009, Chheda and Dumesic, 2007).

Lansalot-Matras and Moreau (2003) began the development of using ionic liquids in the conversion of carbohydrates to 5HMF involving imidazolium salts. Ionic liquids were studied in the presence of catalysts (Chan and Zhang, 2009), no catalysts (Zhao et al., 2007) and in combination with other solvents (Moreau et al., 2006). Despite the high yields achieved in shorter reaction times and moderate reaction temperatures, the high cost of ionic liquids, the fact that they are unstable at high temperatures, and the problem of 5HMF separation as a result of its high solubility in ionic liquids have all been factors in limiting the development of this method (Teong et al., 2014).

Despite the massive investigation work which has been carried out in 5HMF production, the commercialisation of 5HMF production has not yet been achieved, partly due to the lack of an inexpensive production process and partly because the separation of 5HMF as a final product is still a challenge (Saha and Abu-Omar, 2014). The only reported commercial trial was carried out in February 2014 by AVA Biochem in Muttenz,Switzerland, with a small production capacity of 20 ton/year, with purity of

99.9%, by implementing a hydrothermal carbonisation process, where the feedstock of biomass was converted in an aqueous media to coal under pressure and temperature of 220 °C. Then, the hydrogen cations and hydroxide anions were removed via an anaerobic chemical process (Biochem, 2014).

With regard to the drawbacks of the aforementioned systems, this PhD thesis addresses the use of novel Deep Eutectic Solvents (DESs), which have not been used for dehydration reactions before. Here, the DESs are used as green and self-catalysed media for the dehydration of fructose to 5HMF with no need to add water to dissolve the fructose and with no external catalyst as the acid used is both a hydrogen bond donor (HBD) and a catalyst at the same time. DESs are new forms of ionic liquids, discovered by Abbott in 2003 and obtained from renewable resources. They are mixtures formed by mixing any quaternary ammonium salt with HBDs such as amides, amines, alcohols or carboxylic acids. DESs are cheaper and more environmentally friendly than normal ionic liquids.

1.4.5 Properties of Deep Eutectic Solvents

DESs are chemically self-associated solvents of two or three safe components aided by hydrogen bond donors (HBD) interactions to form a eutectic mixture of lower melting point than the individual components. They are mostly liquids at temperatures below 100 ºC. In addition to been environmentally friendly, they have shown physico-chemical properties that is similar to ionic liquids (Zhang et al., 2012b). In order to formulate and develop new DES, it is important to review and understand the physico-chemical properties of some DESs reported in the literature. Table 1.3 summarises typical properties of some formulated ChCl based DESs with variety of HBDs such as; urea (U), ethylene glycol (EG), glycerol (G), thiourea (TU) and trifluoroacetamide (TFA) that have been reported in the literature.

Table 1.3. Properties of some selected ChCl based DESs

DES	Salt:HBD (molar ratio)	Melting point °C	Viscosity (cP)	Density (g cm^{-3})	Surface tension (mN m^{-1})	Conductivity (mS cm^{-1})	Polarity (kJ mol^{-1})	Reference
ChCl-U	1:2	12	750 (25 °C)	1.25	52	0.199 (40 °C)	-	(Abbott et al., 2006)
ChCl-TU	1:2	69	-	-	-	-	-	(Abbott et al., 2003)
ChCl-EG	1:2	-66.01	37 (25 °C)	1.12	48.9	7.6 (20 °C)	-	(Shahbaz et al., 2012)
ChCl-G	1:2	-36.15	259 (25 °C)	1.18	57.24	1.05 (20 °C)	243.84	(Abbott et al., 2011)
ChCl-G	1:3	-32.65	450 (20 °C)	1.2	-	-	242.51	(Abbott et al., 2007)
ChCl-TFA	1:2	-	77 (40 °C)	1.34	35.9	0.286 (40 °C)	-	(Abbott et al., 2006)
ChCl-1,4-butanediol	1:3	-32	140 (20 °C)	1.06	47.17	1.64 (20 °C)	-	(Shahbaz et al., 2012)

The properties of interest are commonly melting and freezing temperatures, density, viscosity, polarity, conductivity, surface tension and vapour pressure. DESs can be prepared easily in the laboratory by mixing high melting components such as ammonium or phosphonium salt and a neutral compound which is able to associate through hydrogen bond interactions such as amides, alcohols, carboxylic acids, phenols and carbohydrates (Cardellini et al., 2014). This HBD association lowers the melting point of the mixture significantly.

The choline chloride (ChCl)/urea DES, was the first to be formulated, commonly used and studied. The most commonly used molar mixture ratios of ChCl:urea is 1:2 (Table 1.3). In this study, the DESs were developed using ChCl, Diethyl Ethanol Ammonium Chloride (DEAC), p-Toluene Sulphonic Acid (p-TSA) and Adipic acid. The mixture of two of these components formed the following DESs ChCl-p-TSA, DEAC-p-TSA and ChCl-Adipic. Figure 1.8 shows the phase diagram of a eutectic point on a two components mixture. Depression of freezing point (ΔTf) represent the magnitude of the interaction between A + B as shown in Figure 1.8, which is controlled by the difference in the freezing point at the eutectic composition of the mixture A + B rather than the theoretical ideal mixture (Smith et al., 2014). Hence, the more the interaction, the larger the value of ΔTf. For example, the individual melting point of ChCl as an organic salt is 302 °C. This salt cannot be used as a solvent in its solid state as it is not possible to produce 5HMF at this severe reaction temperature, since degradation of 5HMF would occur. On the other hand, the melting point of the p-TSA as an acid catalyst is 103.5 °C. This clearly shows the necessity of using a higher temperature and/or a solvent such as water or an organic solvent to dilute the acid.

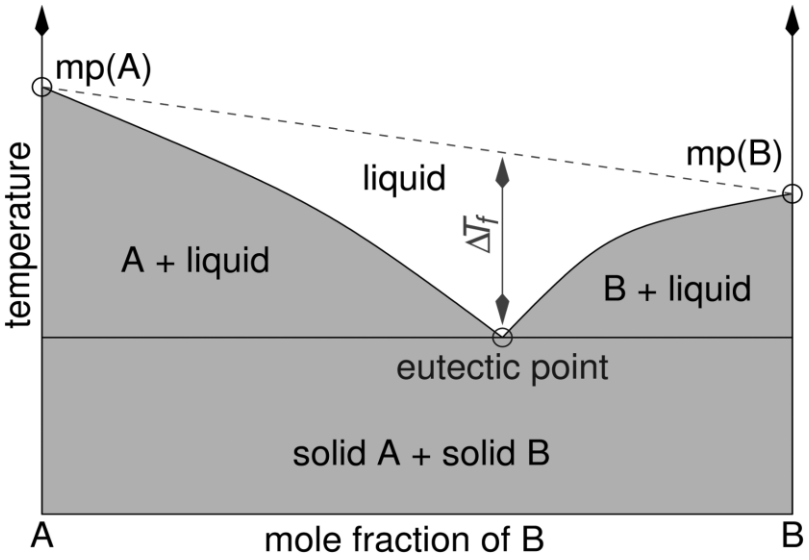


Figure 1.8. Phase diagram of binary DES system (Smith et al., 2014)

1.5 Aim and Objectives of This Thesis

The aim of this work is to produce 5HMF from a fructose dehydration reaction using a novel DES combination that has the dual function of green solvent and catalyst. 5HMF is a precursor to produce biofuel and high-value chemicals. To increase the yield of 5HMF from the dehydration of fructose with resultant environmental and economic benefits, the project therefore seeks to address the following specific objectives:

- To prepare DESs that are biodegradable, renewable, and environmentally friendly using Choline chloride (ChCl), diethylenethanol ammonium chloride (DEAC), para-toluene sulphonic acid (p-TSA) and adipic acid. Three different DESs were formulated using these acids and salts, namely a) DES (ChCl and p-TSA), b) salt-modified DES (DEAC and p-TSA) and c) acid-modified DES (ChCl and adipic acid).

- To test the ability of the prepared DESs to perform the dual function of catalyst and solvent in the dehydration reaction of fructose to 5HMF.

- To evaluate the effect of the reaction factors of temperature, reaction time, fructose-to-DES ratio (feed ratio), and the DES composition molar mixing ratio (acid-to-salt) on the dehydration reaction of fructose to 5HMF, and to determine the best reaction conditions.

- To investigate the effect of DES composition for the three formulated DESs on the optimum yield and selectivity of 5HMF, and on the conversion of fructose from the dehydration reaction.

- To study the reaction kinetics of all three DES systems in order to understand the rate of fructose conversion and to determine the reaction order, rate constant and the activation energies of each system.

1.6 Thesis Layout

This thesis consists of nine chapters. Chapter One covers the introductory background, the motivation for the research and finally the specific objectives to be accomplished in the project. Chapter Two is the literature review, which addresses previous research on 5HMF production using different catalysts, solvents and different biomass sources. A general background about the synthesis, properties and applications of DES solvents is also presented. Chapter Three details the materials and methods used in this study. They include feedstock, DES preparation techniques, measuring instruments and the experimental setup.

The effects of reaction temperature, reaction time, feed ratio and molar mixing ratio on the dehydration reaction of fructose to 5HMF using the DES (ChCl and p-TSA) are presented and discussed in Chapter Four. The results of similar experiments using a salt-modified DES (p-TSA and N,N-diethylenethanol ammonium chloride) (DEAC) and an

acid-modified DES (adipic acid and ChCl) are presented and discussed in Chapters Five and Six, respectively. The three different DESs examined for the dehydration reactions of fructose to 5HMF are summarised, as shown in Figure 1.9.

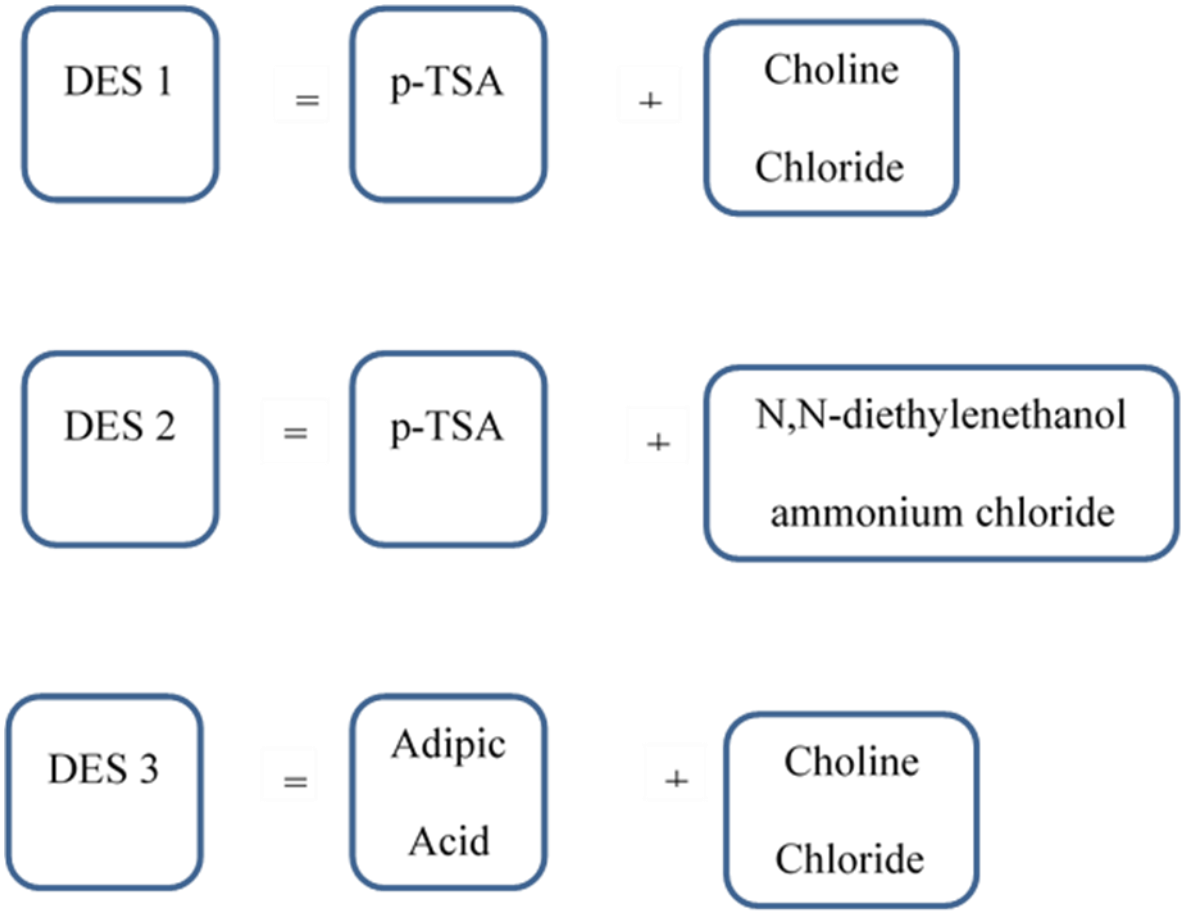


Figure 1.9 Experimental work layout

In Chapter Seven the kinetics of the three DES systems studied to determine the reaction order, the reaction rate constant and the activation energy of each system are presented and discussed. Chapter Eight is a comparison study of the three DES systems and highlights the main differences in the observations and results obtained. The effects of the acids and salts in the different DES formulations on the fructose dehydration reaction to 5HMF are also presented in Chapter Eight. Finally, Chapter Nine summarises the conclusions of the work and outlines recommendations for future research.

Chapter 2 Literature Review

2.1 Overview

This chapter gives an overview of the dehydration reaction chemistry and the systems used in converting different biomass resources to 5HMF. The recent archived results and reaction conditions of the different systems are highlighted and compared. This chapter also discusses the nature of the DESs and highlights their properties and applications.

2.2 The Chemistry of the Dehydration Reaction of Fructose to 5HMF

Dehydration of fructose is generally defined as the elimination of three molecules of water from the substrate. This reaction is usually performed in the presence of an acid catalyst as a proton donor and a solvent as a reaction medium.

Fructose dehydration reaction mechanisms were first reported by Haworth and Jones (1944). They proposed that it is a cyclic form of fructose, which leads to the formation of 5HMF. This was also suggested by (Antal et al., 1990), who stated that the 5HMF formation is favoured to go through a fructofuranose ring. The same group also proposed that the fructose transformation to 5HMF could be done over an open ring pathway. This pathway was not preferred, due to the high activation barriers involved in open ring pathways (Nimlos et al., 2006). Several studies have been carried out in aqueous media to investigate the mechanisms of the fructose dehydration reactions to 5HMF (Amarasekara et al., 2008). All these studies focused on the transformation of fructose to 5HMF, rather than the different intermediates produced. Amarasekara et al. (2008) conducted a nuclear magn**etic** resonance (NMR) study of a fructose dehydration reaction catalysed by DMSO. This study concluded that the dehydration of fructose occurs in two furanose forms of D-fructose by the elimination of three molecules of water. Caratzoulas and Vlachos (2011)

studied the closed ring mechanism which is illustrated in Figure 2.1, and stated that the dehydration of fructose is accomplished by removing three different water molecules in an acidic medium.

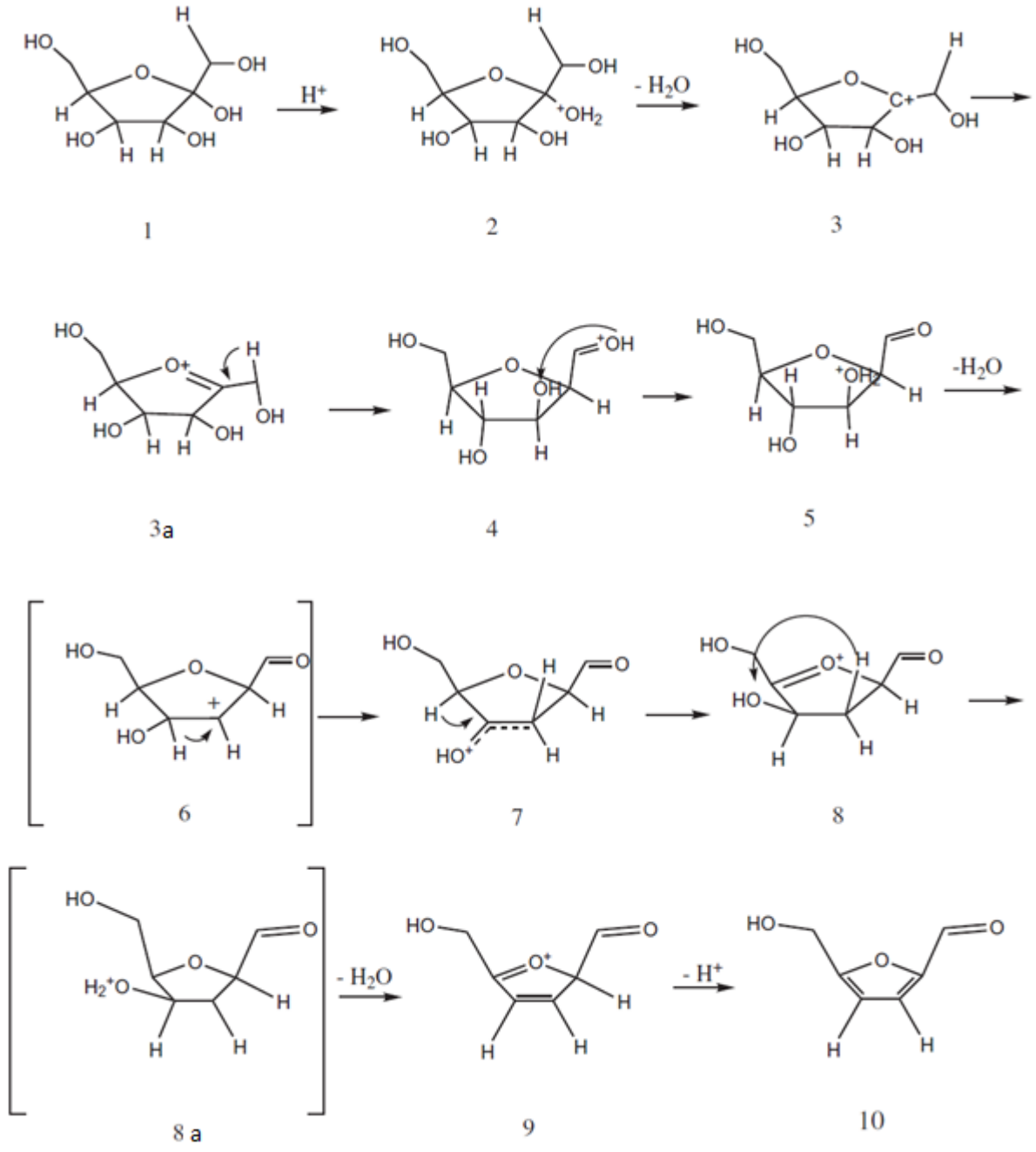


Figure 2.1. Fructose dehydration to 5HMF mechanism (Caratzoulas and Vlachos, 2011)

The closed ring mechanism of fructose dehydration to 5HMF starts by the protonation of the OH group attached to the second carbon atom in step 1, as shown in Figure 2.1, and transforming it to a water molecule, as shown in step 2. This is followed by the removal of the protonated OH in a form of a water molecule from the second carbon atom to form a stable intermediate in step 3a, where a charge is transported from oxygen atom no. 5 to carbon atom no. 2, and both atoms are bound by a double bond.

The second dehydration step is performed through three actions. Firstly, a hydride transfer happens from carbon atom no. 1 to carbon atom no. 2, as shown in steps 3a and 4. Secondly, a proton transfer between the oxygen atoms no. 1 and no. 3 results in the formation of an oxonium ion, as shown in steps 4 and 5 in Figure 2.1. Thirdly, a dehydration action occurs, as illustrated in steps 5 and 6. As the intermediate formed in step 6 is unstable, a hydride transformation from carbon atom no. 4 to carbon atom no. 3 occurs spontaneously during the second dehydration step (from step 6 to step 7) in Figure 2.1.

The third dehydration step occurs by a hydride transformation to the carbon atom no. 4, corresponding to the transfer from step 7 to step 8, followed by a proton transfer from carbon atom no. 3 to oxygen atom no. 4 to form an oxonium ion, as shown in steps 8 and 8a. As the intermediate formed in step 8a is unstable, once the proton is received by oxygen atom no. 4 the bond between carbon atom no. 4 and oxygen atom no. 4 breaks off and the water molecule immediately leaves the ring, as shown in steps 8a and 9. This is followed by deprotonating from step 9 to step 10.

2.3 The Proposed Side Reactions Occurring with the Dehydration Reaction of Fructose to 5HMF

The lack of sustainability and the high cost of the production processes of 5HMF pose a challenge for the commercialisation of production (Melo et al., 2014). Optimisation of the industrial scale process remains the focus of ongoing research. Tao et al. (2011) suggested that the main side reactions associated with the dehydration reaction of fructose to 5HMF are the rehydration of 5HMF to formic and levulinic acids, the condensation reactions caused by the single polymerisation of 5HMF molecules to produce soluble humins, or the cross-polymerisation between fructose and 5HMF molecules to produce insoluble humins, as shown in Figure 2.2. The same study proved that a small amount of furfural was produced from 5HMF at the same reaction conditions.

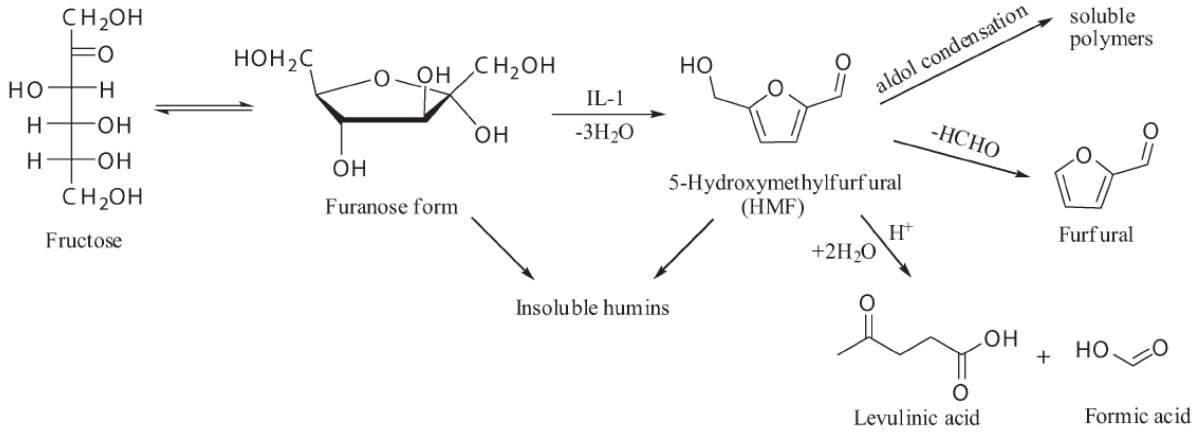


Figure 2.2. The pathway of fructose dehydration to 5HMF and possible side reactions (Tao et al., 2011)

These side reactions are the main reason for the low yield and selectivity of 5HMF. The occurrence of these side reactions is directly connected to the nature of the production process and its conditions. For instance, Tao et al. (2011) studied the dehydration of

fructose using an acidic ionic liquid as a catalyst and a biphasic system consisting of water/MIBK as a reaction medium. It was reported that when the reaction was carried out in an aqueous medium, the rehydration of 5HMF to formic and levulinic acids is the most probable pathway of the side reaction. Prolonging the reaction time and increasing the reaction temperature may lead to the occurrence of the condensation reactions of 5HMF to produce polymers or the cross-polymerisation between fructose and 5HMF to produce humins. Increasing the mass of the substrate fructose could lead to a cross-polymerisation or condensation of 5HMF and produce humins and polymers. In Tao et al. (2011) study, it was also reported that the side reactions were activated by increasing the dosage of the catalyst, which led to a decrease in the fructose conversion and the 5HMF yield. In another study, the conversion of glucose in DMAC as a solvent and $AlCl_3$ as a catalyst was reported. It was found that increasing the reaction temperature and prolonging the reaction time produced a brown substance, which could be humins (Ren et al., 2014).

2.4 Production of 5HMF in Different Systems

Over the last decade, 5HMF has been produced on a laboratory scale using different systems. In the following sections, the various systems reported in the literature are described.

2.4.1 Production of 5HMF in an Aqueous System using Homogenous Catalysts

In the aqueous system, water acts as a green reaction medium without the use of catalysts. Compared to other solvents, water can dissolve high concentrations of sugars, while it is cheap, abundant, and environmentally friendly (Van Putten et al., 2013). Despite these advantages, the dehydration of fructose with water as a reaction medium was limited by the severe reaction conditions required, and also by a low yield of 5HMF due to rehydration resulting in by-products such as formic and levulinic acids. Table 2.1 shows

some previous studies on different initial fructose concentrations, which were dehydrated to 5HMF in water without a catalyst. It can be observed that the yield of 5HMF was low, despite the high reaction temperatures used.

Table 2.1. Fructose dehydration in an aqueous system without using any catalyst

Fructose Con.	Temp. °C	Reaction time (min)	Fructose conversion (%)	5HMF yield (%)	5HMF select. (%)	Ref.
30 wt%	160	5	5	1	28	(Hansen et al., 2009)
11 wt%	200	30	89	51	57	(Li et al., 2009)
0.9 wt%	350	1	67	8	11	(Aida et al., 2007)
55 mM	180	60	87	47	65	(Moller et al., 2012)

To overcome the low yields obtained from the aqueous system without a catalyst, different organic and inorganic acids were studied as homogeneous catalysts for the dehydration of fructose to 5HMF. Table **2.2** shows 5HMF yields reported using different acid catalysts in subcritical water (Asghari and Yoshida, 2007). The highest yield obtained is 65.3 % (H_3PO_4), which is relatively low due to the presence of water, despite the high reaction temperature (240 °C). The quest to increase the 5HMF yield from fructose dehydration has necessitated the investigation of alternative reaction media to resolve the challenges of rehydration caused by water.

Table 2.2. The use of homogeneous catalysts in an aqueous system to catalyse fructose dehydration to 5HMF at pH of 2, reaction time of 2 min and reaction temperature of 240 °C

Catalyst	5HMF yield (mol%)
HCl	29.6
H_2SO_4	40.3
H_3PO_4	65.3
Maleic acid	60.3
Citric acid	17.6
Oxalic acid	17.4
Uncatalysed	18.1

In another study, a mixture of acid and base catalyst (composed of H_3PO_4 and NaOH) was used to catalyse the conversion of different carbohydrates to 5HMF with compressed hot water as the reaction medium (Daorattanachai et al., 2012). 5HMF yields of 9.6% and 29% were obtained from glucose and fructose, respectively, for a reaction temperature range of 200 – 230 °C and reaction time of 5 min. Meanwhile, a 5HMF yield of 7.5% was achieved by the same authors from cellulose with a conversion of 23%. It can be observed that the yields of 5HMF obtained using fructose as a starting material were high compared to glucose and cellulose. This can be attributed to the ease with which fructose can be dehydrated to 5HMF when compared to glucose, which requires an isomerisation process prior to dehydration. Furthermore, the purpose of using NaOH as a

catalyst is to improve the conversion of glucose to fructose, and thus increase the 5HMF yield. Despite the short reaction time and the slight improvement in 5HMF yields compared to the non-catalysed aqueous system, the development of the aqueous system with homogeneous catalysts is faced with the challenges of high reaction temperatures, the difficulties of recovering the homogeneous catalysts and the relatively low yields caused by the rehydration of 5HMF because of the presence of water as a solvent.

To resolve the rehydration challenges, Wang et al. (2014) reported on the dehydration to 5HMF using a mixture of glucose and fructose with a homogeneous hydrochloric acid catalyst and a mixture of water and acetone as a continuous extraction solvent. They observed a 5HMF selectivity of 70%. The same authors reported that Chitin biomass, namely glucose amine (GLc NH_4), was converted to 5HMF in an aqueous solution containing 67% $ZnCl_2$, achieving a 5HMF yield of 21.9% at 120 °C with 99% feed conversion. The role of acetone was to aid the extraction of 5HMF from the aqueous to the organic phase, which remarkably improved the 5HMF yield compared to that obtained in a previous study by (Daorattanachai et al., 2012). The study by Wang et al. (2014) would have been more interesting if a green solvent had been used and a higher yield of 5HMF accomplished. Nevertheless, the high flammability and the ecological effect of acetone still pose a challenge to the scaling up of the production process.

The homogeneous catalysts were also investigated as co-catalysts with heterogeneous catalysts. In this respect, Yang et al. (2013) suggested the addition of HCl to improve the catalytic activity of a heterogeneous $AlCl_3$. This efficiently promoted the conversion of glucose to 5HMF in a biphasic system composed of water and THF, producing a 62% yield of 5HMF. In a similar way, Binder and Raines (2009) reported the conversion of lignocellulosic biomass to 5HMF in a mixture of DMA and LiCl as a

solvent and catalysed by HCl and $CrCl_2$, giving a 5HMF yield of 54% in 120 min at 140 °C. In the same work, fructose dehydration to 5HMF catalysed by sulphuric acid in DMA-LiCl as a solvent produced a 5HMF yield of 68% at 120 °C in 60 min. It can be noticed that the ineffectiveness of heterogeneous catalysts was resolved by adding mineral acids to improve them, thus incurring an additional cost. This makes the dehydration process complex in terms of homogeneous catalysts' separation. In addition, the catalysts are non-environmentally friendly. The severe reaction conditions still pose a challenge for the development of this system.

Generally, it is observed that increasing the concentration of substrate in the dehydration reactions of carbohydrates to 5HMF activates side reactions, which decrease the 5HMF yield. In this context, Roman-Leshkov et al. (2006) improved the 5HMF yield obtained from a concentrated solution of fructose (50 wt%) by using a biphasic system composed of an aqueous phase and DMF, catalysed by HCl. The 5HMF produced was continuously extracted by the organic phase composed of MIBK and 2-butanol, as shown in Figure 2.3; 5HMF yield of 80% with fructose conversion of 90% was achieved at 180 °C in 3 min. While a high 5HMF yield was obtained, this system required severe reaction conditions.

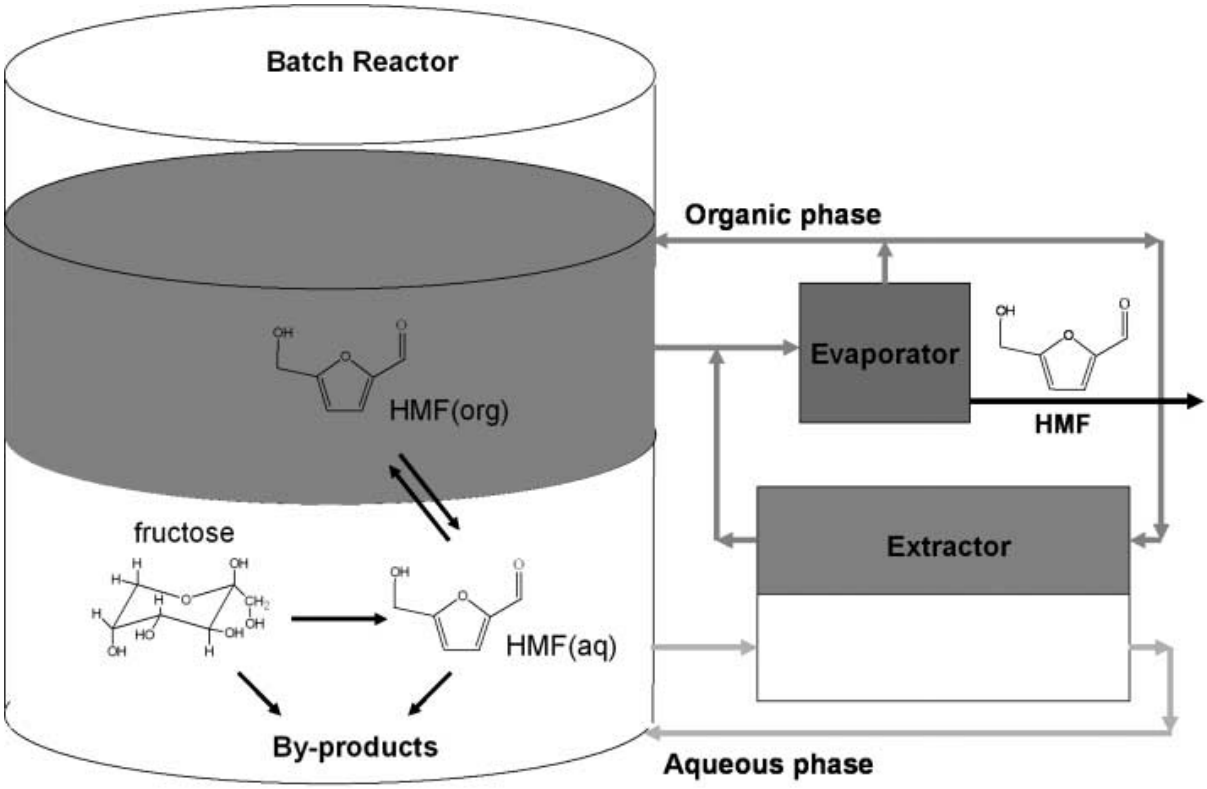


Figure 2.3. Illustration of the batch process in a biphasic system to produce 5HMF from fructose (Roman-Leshkov et al., 2006)

To enhance the extraction process, Roman-Leshkov and Dumesic (2009) stated that the addition of inorganic salts improved the continuous phase extraction of 5HMF in the dehydration of 30 wt% fructose solution. The study was conducted in a biphasic system using 1-butanol as an extraction solvent, catalysed by HCl and H_2SO_4 at 180 °C, reaction time range from 8 to 15 min, volume ratio of organic to aqueous (Vorg/Vaq) of 3.2 and pH of 6. The results are illustrated in Table 2.3. The variation in results was attributed to the ionic interaction between the mixture components and the process parameters such as temperature, pressure, and concentration.

Table 2.3. The effect of different salts on the dehydration of a concentrated fructose solution at reaction temperature 180 °C, pH 6 and time range 8 – 15 min (Roman-Leshkov and Dumesic, 2009)

Salt	Acid	Conversion (%)	Selectivity (%)	R
No salt	HCl	77	69	1.7
LiCl	HCl	71	72	2.2
KCl	HCl	89	84	2.7
NaCl	HCl	87	82	3.1
$CsCl_2$	HCl	92	80	2.5
$CaCl_2$	HCl	77	73	2.2
$MgCl_2$	HCl	78	74	2.3
KBr	HCl	77	71	1.7
NaBr	HCl	90	73	1.9
Na_2SO_4	H_2SO_4	62	71	8.1

Note: R is the HMF concentrations ratio in the organic and aqueous phases.

Homogeneous catalysts were also involved in converting different biomass sources to 5HMF combining an aqueous system with other solvents. Glucose, xylose and fructose were dehydrated to 5HMF in a biphasic reactor containing an aqueous phase with DMSO and an organic phase for extraction composed of MIBK and 2-butanol in the ratio 7:3 w/w. The reaction was conducted at 170 °C and catalysed by different mineral acids HCl, H_2SO_4 and H_3PO_4. The highest 5HMF selectivity achieved was 53%, 91% and 89% from the dehydration of glucose, xylose and fructose, respectively, when the reactions were catalysed by HCl (Chheda and Dumesic, 2007). The main drawbacks of this system were the severe reaction conditions.

Some studies have shown that the type of substrate and the nature of the production system can impact the conversion process. For example, Amiri et al. (2010) conducted a

hydrolysis of rice straw agricultural waste, as an abundant and cheap biomass in a single aqueous phase with 0.5% of sulphuric acid for 180 min at 180 °C, where a 5HMF yield of 15.3 g/kg straw was obtained. The same authors examined different extraction solvents, where the results revealed that a 5HMF yield of 59g/kg straw was achieved when 2-PrOH and BuOH were used as extraction solvents. Despite the severe reaction conditions and the ecological effect of the solvents and catalysts used, the yield obtained was still relatively low. Brasholz et al. (2011) described the dehydration of fructose as a substrate to produce 5HMF. The dehydration was carried out in 0.25 M aqueous HCl and MIBK, using a biphasic continuous flow dehydration system at a flow rate of 0.33 ml/min, as shown in Figure 2.4. This process required less harsh reaction conditions, and a better 5HMF yield of 74% was obtained at 140 °C in 15 min compared with the study reported by (Amiri et al., 2010), which used a different substrate.

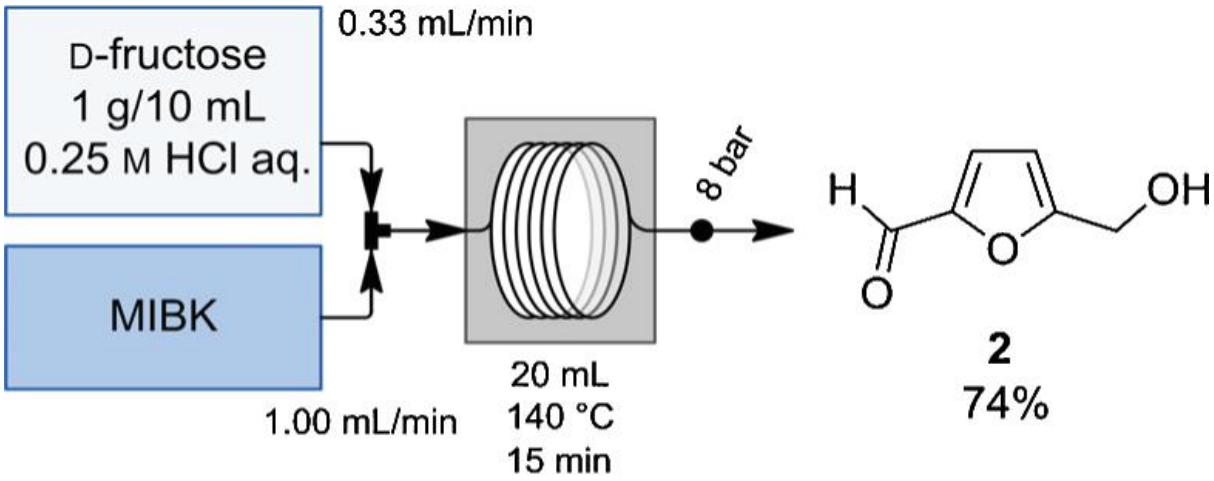


Figure 2.4. Fructose dehydration to 5HMF in a continuous flow biphasic system (Brasholz et al., 2011)

Furthermore, Pagan-Torres et al. (2012) reported glucose conversion to 5HMF in a biphasic system composed of water/2-butylphenol, catalysed by a catalyst mixture of HCl

and $AlCl_3$. They obtained a 62% yield of 5HMF and over 97% of the 5HMF produced was extracted by the organic phase. However, the use of glucose as a substrate requires an isomerisation step, as illustrated in Figure 2.5. This accounts for the relatively low yield obtained compared with that achieved from fructose.

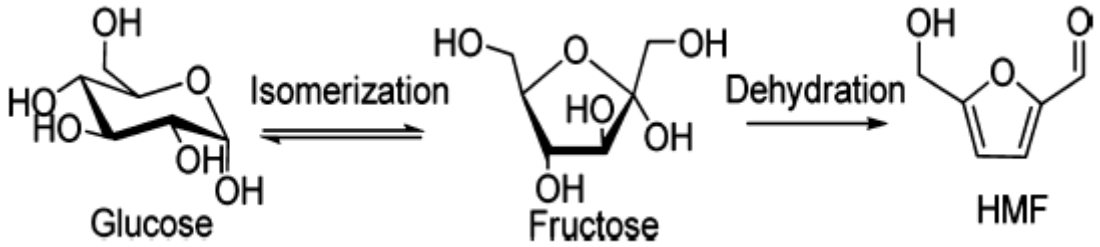


Figure 2.5. Glucose conversion to 5HMF in biphasic system (Pagan-Torres et al., 2012)

Wheat straw was converted to 5HMF in acid catalysis using a microwave. A low 5HMF yield of 3.4% was obtained at a reaction temperature of 170 °C and reaction time of 40 min (Yemiş and Mazza, 2012). A biomass source in the form of girasol (as inulin source) and potato (as starch source) was converted to 5HMF in an ionic liquid of [OMIM]Cl at a reaction temperature of 120 °C and reaction time of 120 min. A 5HMF yield of 54.4% was obtained from a potato when the reaction was catalysed by HCl and $CrCl_2$. On the other hand, 5HMF of 58.2% was obtained from girasol at the same reaction conditions without adding the $CrCl_2$ (Yi et al., 2012). These studies were conducted to convert different forms of biomass to 5HMF in a one pot process and highlighted some drawbacks such as the ecological effects and 5HMF separation difficulties that arise from the combination of mineral acids and ionic liquids used as reaction media. In addition, the severe reaction conditions and the low yields make these processes unfeasible.

Despite the essential role played by mineral acids as catalysts for sugars' conversion to 5HMF, the use of aqueous systems catalysed by homogenous catalysts is associated with several drawbacks. The difficulties include catalyst separation, the limitation of reusability and the necessity for severe reaction conditions (which can activate corrosion) to achieve high 5HMF selectivity. Furthermore, the huge amount of acid waste causes severe negative ecological and environmental effects, while the aqueous phase leads to the activation of side reactions, which causes rehydration of 5HMF to produce formic acid and levulinic acid (Deng et al., 2015). As a result of these disadvantages, more focus was given to the use of solid acids in biomass conversion to 5HMF.

2.4.2 Production of 5HMF from Biomass Catalysed by Solid Catalysts

Solid or heterogeneous catalysts are porous materials with a large surface area. They are capable of accelerating chemical reactions on their surfaces. Some of their advantages are that they are reusable and remain stable under severe reaction conditions (Lin and Huber, 2009). Despite the high 5HMF yields obtained from the dehydration of fructose and the ease of separation, as shown in Table 2.4, the use of solid catalysts in biomass dehydration reactions requires a solvent such as DMSO, which causes difficulty in the separation of 5HMF since their boiling points are in a similar range. Also, these systems require relatively high reaction temperatures and long reaction times, which makes the process unviable. In addition to the previously mentioned challenges, solid catalysts use water as a reaction media, which causes the rehydration of 5HMF.

Table 2.4. Fructose dehydration in solid catalysts

No.	Substrate	Catalyst	Solvent	Temp. (°C)	Time (min)	Fructose conversion %	5HMF yield %	Ref.
1	Fructose	Fe_3O_4, R-SO_3H, COOH (components are specified in abbreviation list)	DMSO	130	40	100	81.1	(Hu et al., 2015)
2	Fructose	Fe_3O_4 and sulfonic acid	DMSO	110	180	99	82	(Zuo et al., 2014)
3	Fructose	$NbCl_5$	(BMIM)Cl	80	30	-	79	(Mittal et al., 2012)
4	Fructose	$Sc(OTf)_3$	DMSO	120	120	100	83.3	(Zhao et al., 2011)
5	Fructose	Zirconium phosphate	Sub-critical water	240	-	80	61	(Hu et al., 2008)
6	Fructose	Sulfonated zirconia	DMSO and acetone	180	20	93.6	72.8	(Zhang et al., 2009)
7	Fructose	Sulfonic acid resin	DMSO	147	60	-	93	(Morales et al., 2014)
8	Fructose	Zeolite	(BMIM)Cl	150	50	-	86.6	(Hu et al., 2014)

Different substrates of biomass were converted to 5HMF in different solid catalysts, as listed in Table 2.5. The results showed that the use of these substrates produced lower yields of 5HMF compared with the fructose reported in Table 2.4. This is due to the deficiency of the solid catalysts to catalyse other required processes such as the isomerisation of glucose to fructose before the dehydration of fructose to 5HMF.

Table 2.5. Conversion of other biomass sources to 5HMF in solid catalysts

No.	Substrate	Catalyst	Solvent	Temp. (°C)	Time (min)	Conversion %	5HMF yield %	Ref.
1	Glucose	Sulfonic group	Water and THF	180	240	99.9	80.7	(Chen et al., 2016)
2	Glucose	Silica	Water and MIBK	195	150	87	36	(Jimenez-Morales et al., 2015)
3	Glucose	Sulfonic acid resin	DMSO	147	1440	-	33	(Morales et al., 2014)
4	Glucose	Silica with zirconium	Water/MIBK	175	150	69	23	(Jiménez-Morales et al., 2014)
5	Glucose	NaI and $AlCl_3$	DMAC	130	15	86	62	(Ren et al., 2014)
6	Glucose	LCC	DMSO and [Bmim]Cl	160	50	99	68	(Guo et al., 2012)
7	Starch	SO^{2-}_4/ZrO_2-Al_2O_3	Water and DMSO	150	360	-	55	(Yang et al., 2012)

It can be noted from Table 2.4 (entry 7) and Table 2.5 (entry 3) that Morales et al. (2014) conducted two experiments using the same system but starting with different substrates, namely fructose and glucose. A lower yield of 5HMF was obtained from glucose, in spite of the longer reaction time used. Entry 1 in Table 2.5 shows a recent study conducted by Chen et al. (2016) investigating a sulfonic acid catalyst which has Brønsted acid and Lewis acid sites for the conversion of glucose to 5HMF. Although they found a high fructose conversion and 5HMF yield, the challenges associated with the use of water and THF were still observed. On the other hand, low yields of 5HMF were obtained for the rest of the heterogeneous catalysts and solvents reported in Table 2.5, despite the relatively high temperatures used.

2.4.3 Production of 5HMF from Biomass in Organic Solvents

Organic solvents have been widely used in the conversion of biomass to 5HMF. Their role is essentially to extract the produced 5HMF to prevent its rehydration. The addition of MIBK during the dehydration reaction of fructose to 5HMF catalysed by zeolites increases the reaction selectivity towards 5HMF. This is due to the role played by MIBK, which fills the pores of the catalyst and, as a consequence, inhibits the side reactions that lead to humins' formation (Ordomsky et al., 2012). Another group (Sampath and Kannan, 2013) conducted a comparison study between the activity of Amberlyst-15 in DMF and DMSO for fructose dehydration to 5HMF. The results revealed that there was a significant loss in Amberlyst-15 activity when DMF was used, while there was no activity loss observed in the DMSO case. It is suggested that activity loss may be caused by the neutralisation of acid sites forming ammonium ions. Despite the high efficiency of DMSO as a solvent for converting biomass to 5HMF, its use was limited by its high boiling point, high flammability and toxicity. Different studies reported the use of

organic solvents as reaction media for the conversion of biomass to 5HMF, as depicted in Table 2.6. Even though the results obtained from the use of organic solvents in sugars' dehydration to 5HMF were much better compared to the ones obtained from aqueous systems, the use of organic solvents as reaction media is faced with several disadvantages, such as the non-green nature, the relatively high cost, and the low solubility of sugars in them.

Table 2.6. The conversion of biomass in organic solvents

Substrate	Organic solvent	Catalyst	Temp. (°C)	Time (min)	Conversion %	5HMF yield %	5HMFselectivity %	Ref.
Fructose	DMSO	Nb_2O_5	120	120	100	86.2	-	(Zhou et al., 2014a)
Fructose	DMSO	-	150	-	-	92	-	(Despax et al., 2013)
Inulin	DMSO	-	150	-	-	47	-	
Fructose (15 wt%)	Glycerol	-	150	3	78	-	4	(Despax et al., 2014)
	Ethylene glycol			15	76		9	
	DMSO			10	100		71	
	DMA			8	87		25	
Fructose	DMSO	[CMIM]Cl	120	120	-	95.7	-	(Hu et al., 2013)
Inulin				180	-	88.4	-	
Glucose	DMAC	-	120	15	-	52	-	(Ren et al., 2013)
Fructose (50 wt%)	DMSO	Amberlyst-15	120	120	-	100	-	(Shimizu et al., 2009)

Apart from the capability of DMSO to self-catalyse the conversion of sugars to 5HMF without additional catalysts, the results illustrated in Table 2.6 show that the use of some organic solvents without catalysts results in low yields of 5HMF. This clearly proves that the use of organic solvents in sugars' dehydration to 5HMF requires catalysts and severe reaction conditions. Furthermore, the non-environmentally friendly nature and the high boiling points of these solvents pose a challenge in the scale-up of the conversion processes.

2.4.4 Production of 5HMF from Biomass in Ionic Liquids

Ionic liquids are a new class of reaction media composed of organic and inorganic ions, first reported in 1914 by (Walden, 1914). Their use as reaction media for the dehydration of fructose to 5HMF is because they offer unique properties such as low vapour pressure, low viscosity, chemical and thermal stability, and low melting point. Moreover, they are capable of dissolving a wide range of sugars (Wang et al., 2014). Therefore, ionic liquids have recently been used in biomass conversion to useful chemicals and biofuels (Van Putten et al., 2013). Comparing the use of ionic liquids as reaction media in biomass conversion to 5HMF with previous systems (aqueous, solid catalyst, and solvents), their use showed higher yields of 5HMF in mild reaction conditions and eliminated the use of water in the reactions. This led to a reduction in side reactions and an increase in 5HMF yields. The selection of an ionic liquid as a reaction medium is subject to its composition, which is highly affected by its properties such as melting point, viscosity and density (Earle and Seddon, 2000). A summary is presented in Table 2.7 of the published results of fructose dehydration to 5HMF in ionic liquids without the addition of catalyst.

Table 2.7. Dehydration of fructose to 5HMF in ionic liquids without catalyst

Ionic liquid	Time (min)	Temp. (°C)	Conv. %	Yield %	Selectivity %	Ref.
[HMIm]Cl	45	90	98	92	94	(Moreau et al., 2006)
[EMIm]Cl	180	120	100	73	73	(Zhao et al., 2007)
[BMIm]Cl	50	120	93	63	68	(Cao et al., 2011)
PyHCl	80	60	92	69	76	(Hu et al., 2008)
[BMIm]Cl	180	80	4	0	0	(Wei et al., 2011)
[BMIm]Cl	180	100	60	28	47	(Wei et al., 2011)

Cao et al. (2011) studied the dehydration of fructose to 5HMF in [BMIm]Cl without the addition of catalyst. At a reaction temperature of 120 °C and a reaction time of 50 min, a conversion of 93% was achieved with 63% yield and 68% selectivity of 5HMF. The relatively higher conversion and yield obtained may be attributed to the catalytic activity of the ionic liquid. Wei et al. (2011) investigated the same ionic liquid at different reaction temperatures and a reaction time of 180 min without a catalyst. The reported results showed that the conversion of fructose increased from 4 to 60% when the reaction temperature increased from 80 to 100 °C. No 5HMF was produced at 80 °C, whereas when the temperature increased to 100 °C a 5HMF yield of 28% and selectivity of 47% were obtained. In another study, Moreau et al. (2006) reported a higher 5HMF yield of 92% and fructose conversion of 98% when [HMIm]Cl was used with no catalyst at mild

reaction conditions of 90 °C and 45 min. This could be due to the improved activity obtained from the different composition of the ionic liquid.

Table 2.8 shows the use of different ionic liquids and catalysts for the dehydration of fructose to 5HMF. Cao et al. (2011) reported a follow-up study on fructose dehydration to 5HMF catalysed by H_2SO_4 in [HMIm]Cl at a reaction time of 50 min and reaction temperature of 100 °C. It was found that increasing the catalyst loading from 10 to 25 mol% increased the conversion of fructose from 55 to 82% and the 5HMF yield from 7 to 100%. Zhang et al. (2011b) investigated fructose dehydration to 5HMF catalysed by $CrCl_2$ in [EMIm]Cl at reaction conditions of 80 °C and 180 min. The full conversion of fructose and 60% yield of 5HMF were obtained. However, the lower yield obtained at a longer reaction time could be attributed to the activity of the catalyst used. Qi et al. (2009b) investigated the same ionic liquid for fructose dehydration to 5HMF in a heterogeneous catalyst of Amberlyer 15. A 5HMF yield of 83% was achieved in a shorter reaction time of 10 min at the same reaction temperature.

Table 2.8. Dehydration of fructose to 5HMF in ionic liquids with homogeneous and heterogeneous catalysts

Ionic liquid	Catalyst	Temp. (°C)	Time (min)	Conv. %	Yield %	Selectivity %	Ref.
[EMIm]Cl	$CrCl_2$ 6 mol%	80	180	100	60	60	(Zhang et al., 2011b)
[BMIm]Cl	$AuCl_3$.HCl 7 mol%	80	180	50	22	44	(Wei et al., 2011)
[BeMIm]Cl	$CrCl_3.6H_2O$ 10 mol%	100	120	100	71	71	(Cao et al., 2011)
[HMIm]Cl	H_2SO_4 10 mol%	100	50	55	7	13	(Cao et al., 2011)
[HMIm]Cl	H_2SO_4 25 mol%	100	50	100	100	82	(Cao et al., 2011)
[BMIm]Cl	Amberlyer 15 100 wt%	80	10	99	83	85	(Qi et al., 2009b)
[EMIm]Cl	PTA/MIL101 40 wt%	80	60	87	80	92	(Zhang et al., 2011a)

More recent studies reported the use of different ionic liquids and catalysts in fructose dehydration to 5HMF. The results of these studies are presented in Table 2.9. Liu et al. (2015) reported that $(NH_4)_2S_2O_3$ efficiently catalysed the fructose dehydration reaction to 5HMF using [Bmim]Cl, achieving 5HMF selectivity of 81.6% at mild reaction conditions. On the other hand, Jadhav et al. (2014) reported a better yield of 5HMF at mild reaction conditions when using active self-catalysed unsymmetrical dicationic ionic liquids. Despite the high yield obtained at mild reaction conditions with no catalyst involved, these systems suffered from the high cost of the ionic liquids involved.

Table 2.9. Fructose dehydration to 5HMF in different ionic liquids and catalysts

Substrate	Ionic liquid	Catalyst	Temp (°C)	Time (min)	Con. %	Yield %	Sel. %	Ref.
Fructose	[Bmim]Cl	$(NH_4)_2S_2O_3$	120	50	-	-	81.6	(Liu et al., 2015)
Fructose	Dicationic ionic liquids	-	70	40	-	92.3	-	(Jadhav et al., 2014)
Fructose	[Bmim]Cl	$H_3PW_{12}O_{40}$	80	5	99	99	99	(Xiao et al., 2014)
Fructose	[Bmim]Cl	$FeCl_3$	100	240	-	90.8	-	(Zhou et al., 2014b)

Xiao and Song (2014) reported that different heteropoly acids showed high activity in catalysing the fructose dehydration to 5HMF in [Bmim]Cl, where a fructose conversion, 5HMF yield and selectivity each of 99% were obtained at 80 °C and 5 min when $H_3PW_{12}O_{40}$ was used as a catalyst. On the other hand, Zhou et al. (2014b) reported a 5HMF yield of 90.8% at severe reaction conditions using the same ionic liquid [Bmim]Cl,

but with $FeCl_3$ as a catalyst. In the same work, the 5HMF yield decreased to 60.3% when a solvent mixture of [Bmim]Cl and ethanol was used. This emphasises how the nature of the catalyst and the reaction medium govern the reaction pathway and also influence the 5HMF yield. Chinnappan et al. (2014) reported that the use of ionic liquids associated with metal complexes in fructose dehydration gave a 5HMF yield of 95.5% at 110 °C and 60 min. Despite the high yield of 5HMF obtained, the commercialisation of this process is limited by the cost of the ionic liquid.

Table 2.10 shows the yields of 5HMF from fructose, cellulose, and sucrose when dehydrated in ionic liquids. It is clear that the yields obtained from cellulose and sucrose are lower compared to the ones obtained from fructose. This could be attributed to the complicated conversion routes of cellulose and sucrose sugars which, unlike fructose, require hydrolysis or pyrolysis at severe conditions and catalysts. Zhou et al. (2015) reported a one-step cellulose conversion to 5HMF using an ionic liquid of [Bmim]Cl, catalysed with $CrCl_3$. The optimum 5HMF yield achieved was 63% at atmospheric pressure and 120 °C. Jadhav et al. (2012) reported a complete conversion of fructose and sucrose when both were converted to 5HMF in an ionic liquid at room temperature. The 5HMF yield obtained from fructose was much higher and at milder reaction conditions compared to the yield from sucrose. Su et al. (2013) reported that the hydrolysis of sucrose in [Emim]Br and amino acids, using tyrosine as a catalyst at harsh reaction conditions resulted in a 5HMF yield of only 76%.

Table 2.10. Conversion of different carbohydrates to 5HMF in ionic liquids

Substrate	Ionic liquid	Catalyst or solvent	Temp. (°C)	Time (min)	Conv. %	Yield %	Sel. %	Ref.
Cellulose	[Bmim]Cl	$CrCl_3$	120	-	100	63	-	(Zhou et al., 2015)
Sucrose	$[TetraEG(mim)_2][OMs]_2$		120	150	100	67.2	-	(Javhav et al., 2012)
Fructose		-	-	40	-	92.3	-	
Sucrose	[Emim]Br	Amino acids, and tyrosine	160	240	-	76	-	(Su et al., 2013)

The isomerisation of glucose was reported in different ionic liquids and catalysts. Some of the studies are shown in Table 2.11, where the results showed lower yields under higher reaction conditions compared to fructose. Tao et al. (2014) reported a 5HMF yield of 75.1% from glucose using a functionalised acidic ionic liquid of SO_3OH in a biphasic system. However, the process required severe reaction conditions. In another work, glucose was converted to 5HMF and catalysed by zeolite in [BMIM]Cl as a solvent. Despite the shorter reaction time used, the 5HMF yield and glucose conversion were not sufficiently high. It was also found that increasing the catalyst loading, reaction temperature and reaction time had a negative effect on the 5HMF yield (Hu et al., 2014). The variation in results between these two studies could be attributed to the activity of the SO_3OH compared to zeolite and the activity of the extraction solvent used. Furthermore, the presence of MIBK enhanced the solubility of glucose and thus improved the conversion rate. On the other hand, the water content and severe reaction conditions negatively influenced the reaction. The composition of the reaction medium is clearly an important issue in achieving higher conversion. Qi et al. (2012) investigated the use of water and an ionic liquid mixture on the conversion of glucose to 5HMF, catalysed by ZrO_2. The results obtained showed a low yield of 5HMF. This was due to the severe reaction temperatures and the presence of water as a solvent. Hu et al. (2012) reported that a double catalytic mixture of boric acid and chromium chloride improved the activity of the catalytic mixture. This promoted the conversion of glucose to 5HMF in an ionic liquid of [Bmim]Cl.

Table 2.11. The conversion of glucose to 5HMF in ionic liquids

Substrate	Ionic liquids	Catalyst or solvent	Temp. (°C)	Time (min)	Con. %	Yield %	Sel. %	Ref.
Glucose	SO_3OH	MIBK and water	120	360	97.4	75.1	-	(Tao et al., 2014)
Glucose	[BMIM]Cl	Zeolite	150	50	80.6	50.3	-	(Hu et al., 2014)
Glucose	1,3-dialkylimidazolium chloride ionic	ZrO_2 and water	200	10	-	53	-	(Qi et al., 2012)
Glucose	[BMIM]Cl	Boric acid and chromium chloride	120	30	-	78.8	-	(Hu et al., 2012)

Generally, the necessity of using external catalysts and solvents for the conversion of biomass to 5HMF, as well as the high cost of ionic liquids, remain the main challenges for developing these systems.

2.5 Deep Eutectic Solvents as New Reaction Media for the Dehydration of Fructose to 5HMF

DESs are new kinds of solvents made by the gentle mixing and heating of any quaternary ammonium salt such as choline chloride (ChCl) with a variety of HBDs in solid form like alcohols, amines, amides and carboxylic acids (Maugeri et al., 2012). This forms a homogeneous eutectic mixture in liquid form at a temperature range of 25 to 70 °C. DESs are characterised by their highly reduced freezing points compared to the individual ones for each component (Zhang et al., 2012b). The chemistry concept of the DES mixtures is that the electrostatic forces between the anions and cations are highly reduced by an interaction between the quaternary ammonium salts and the HBD; thus, the freezing points of the DES mixtures are highly decreased (Maugeri et al., 2012).

The first DES, composed of ChCl and urea was reported by (Abbott et al., 2003). DESs are generally regarded as types of ionic liquids as they share common properties. Despite this similarity in their properties, their structure is completely different. Basically, the DESs are a form of eutectic mixture composed of Brønsted or Lewis acids with different types of bases, which are a source of different ionic and cationic species. On the other hand, ionic liquids consist of one type of anion and cation (Smith et al., 2014).

The drawbacks associated with the use of ionic liquids as solvents are reported to be the poor biodegradability and the toxicity of a variety of ionic liquids (Romero et al., 2008), the impurity of ionic liquids which influence their properties, the environmentally unfriendly synthesis procedures and the high cost. This has discouraged the development

of the use of ionic liquids. In view of such drawbacks, DESs were found to be the optimum alternative solvents, being non-toxic, cheap, biodegradable and renewable (Zhang et al., 2012b). ChCl, which has similarity to vitamin B (Abo-Hamad et al., 2015), is considered the common organic salt used to form a variety of DESs with a large range of HBDs. This is because ChCl is cheap (2 €/kg) (Vigier et al., 2015), renewable and can be obtained by the extraction of biomass and fossil resources (Zhang et al., 2012b). Furthermore, it is biodegradable and non-toxic, as it is used for human food processes and as animal feed (Russ and Konig, 2012). The DESs composed of ChCl are considered economical (Perkins et al., 2014, Singh et al., 2014) and are easy to prepare with no purification or waste disposal required. They are easy to store as they are chemically inert with water, and have no vapour pressure (Zhang et al., 2012b). Also, they are biodegradable, non-flammable and non-toxic (Weaver et al., 2010).

2.5.1 DES Properties

Although the chemical properties of DESs differ from those of ionic liquids, they still share some physical properties such as low vapour pressure, availability in liquid form, and non-flammability (Smith et al., 2014). It was reported that the different DES properties such as density, pH, viscosity and melting point are extremely influenced by the type of the two components that constitute the DES, and their molar mixing ratios (Kareem et al., 2010). In this section, some of the DES properties are discussed.

2.5.2 Freezing Point

DESs are formed by heating and mixing two different solids with individual high melting points that act as HBDs and hydrogen acceptors to form a new mixture in a liquid form with a lower freezing point, as shown in Table 2.12. The results illustrated in Table 2.12 show that the freezing point of the DES mixture is subject to the type of halide salt,

the type of HBD and their molar mixing ratios, while the melting point of the individual components has no influence on the freezing point of the DES. Comparing results 1 and 4 in Table 2.12, the DES freezing point increased from 12 to 51 °C when the HBD changed from urea to acetamide at the same molar ratio. The DES freezing point changed from 51 °C in result 4 to -16 °C in result 6 when the halide salt changed from ChCl to $ZnCl_2$. Changing the molar ratio from 1:2 to 1:1 for the ChCl to urea DES mixture in results 1 and 2 changed the freezing point from 12 to 50 °C, respectively. Both components of the DES in result 2 have the same individual melting points as those in result 5, but the freezing points of the DESs produced are 50 and 10 °C, respectively. It was also reported that the DES freezing point decreased greatly when low molecular weight acids were used as HBDs (Abbott et al., 2004). Despite the limited number of DESs which are liquids at room temperature, DES mixtures with freezing points below 50 °C are preferred for many application fields because they are cheap and green solvents (Zhang et al., 2012b).

Table 2.12. The freezing points of different DESs composed of different halide salts and HBDs (Smith et al., 2014, Zhang et al., 2012b)

No..	Halide salt	Melting point °C (a)	Hydrogen bond donor (HBD)	Melting point °C (a)	Salt to HBD molar ratio	DES Freezing point °C (b)
1	ChCl	303	Urea	134	1:2	12
2	ChCl	303	Urea	134	1:1	50
3	ChCl	303	Adipic acid	153	1:1	85
4	ChCl	303	Acetamide	80	1:2	51
5	ChCl	303	Malonic acid	134	1:1	10
6	$ZnCl_2$	293	Acetamide	80	-	-16
7	$ZnCl_2$	293	Urea	134	-	9
8	$ZnCl_2$	293	Ethylene glycol	-12.9	-	-30
9	methyltriphenylphosphonium bromide	231-233	Ethylene glycol	-12.9	-	- 49.34
10	methyltriphenylphosphonium bromide	231-233	Glycerol	17.8	-	- 4.03
11	benzyltriphenylphosphonium chloride	345-347	Ethylene glycol	-12.9	-	47.91

(a) Melting point is used for the two DES components individually in their solid form.

(b) Freezing point is used to assess the performance of the DES mixture in a liquid form.

2.5.3 Density

Generally, the reported DES densities are slightly higher than water density (Abbott et al., 2006, Abbott et al., 2007). Shahbaz et al. (2011) measured different DES densities using a vibrating tube density meter. Due to the difficulties of measuring the DES densities as a function of temperature, the same group established a prediction method by using the modified Racket's equation, where an error percentage of 1.9 was reported. The density of the DES decreases by increasing the molar ratio of salt to HBD. This is attributed to the free volume in the DES (Shahbaz et al., 2012). The DES mixtures composed of $ZnCl_2$ to urea (1:3.5) and $ZnCl_2$ to acetamide (1:4) have recorded densities of 1.63 and 1.36 g/cm^3, respectively. These densities are higher than the densities of the pure HBDs urea and acetamide, which are 1.16 and 1.32 g/cm^3, respectively (Zhang et al., 2012b). As the DES structure contains holes, this difference was attributed to the decrease in the radius of these holes as a result of mixing the HBDs with $ZnCl_2$, which leads to an increase in the densities of the DESs (Abbott et al., 2007).

2.5.4 Viscosity

The majority of the DESs have a high viscosity, which is close to 100 cP at room temperature. This could be attributed to the reduced movement of the free DES species because of the strong hydrogen bonding between the two components of the DES. Generally, the viscosity of the DESs composed of two components is controlled by the interactions of electrostatic forces, namely the hydrogen bonds and van der Waals forces. In terms of DES applications as solvents, the lower viscosity DESs are preferred as green reaction media (Zhang et al., 2012b). The less viscous solvent is also easier to handle and reduces the process cost as it requires less energy to pump (Gunny et al., 2014). It is also mentioned that low viscosity DES and cellulose mixtures greatly improve the kinetics of

biomass treatment reactions (Gericke et al., 2012). As mentioned above, the DES viscosity is highly affected by the nature of the DES components and the mixing ratios, as well as the temperature. As shown in Table 2.13, in entries 1 and 2 the DES viscosity changed from 750 to 85000 cP when the HBD changed from urea to $ZnCl_2$ at the same molar ratio and temperature. Increasing the temperature from 25 to 40 °C reduced the viscosity of the ChCl/urea DES mixture from 750 to 169 cP, as shown in entries 1 and 3. Changing the ChCl to glycerol DES molar ratio from 1:2 to 1:3 and 1:4 changed the DES viscosity to 376, 450 and 503 cP, respectively, as shown in entries 4, 5 and 6.

Table 2.13. The effect of different parameters on DES viscosity (Zhang et al., 2012b)

No.	Salt	HBD	Salt-to-HBD molar ratio	Viscosity (cP)
1	ChCl	Urea	1:2	750 at 25 °C
2	ChCl	$ZnCl_2$	1:2	85000 at 25 °C
3	ChCl	Urea	1:2	169 at 40 °C
4	ChCl	Glycerol	1:2	376 at 20 °C
5	ChCl	Glycerol	1:3	450 at 20 °C
6	ChCl	Glycerol	1:4	503 at 20 °C

2.5.5 Polarity

Zhang et al. (2011b) investigated the polarity of a DES mixture of ChCl and glycerol by the Richardt Dye method. It was found that the polarity of the DES mixture increased as the concentration of ChCl increased.

2.5.6 Ionic Conductivity

The ionic conductivity of DESs is generally found to be poor (less than 2 mS/cm). This is due to their relatively high viscosity. As a function of viscosity, DES

conductivities increase with increasing temperatures and ChCl content in the DES mixture (Zhang et al., 2012b).

2.5.7 DES Applications

DESs have superior advantages and unique properties such as low vapour pressure, non-toxicity, non-flammability, biodegradability, ease of preparation, availability and low cost compared with conventional ionic liquids. Thus, the involvement of DESs in many applications has been of great interest over the last decade (Abo-Hamad et al., 2015). In addition to their use as alternative reaction media in organic synthesis, DESs are also widely involved in many applications in the research field (Smith et al., 2014) such as nanotechnology (Wagle et al., 2014, Zhang et al., 2015a), electrochemistry (Xu et al., 2015b, Renjith and Lakshminarayanan, 2015) , resin catalyst manufacturing (Lian et al., 2015), extraction of natural products (Nam et al., 2015), batteries (Xiong et al., 2015), corrosion prevention (Fashu et al., 2015, Zhang et al., 2015b), bio and metal catalysis (Zhao et al., 2015), biodiesel production (Gu et al., 2015, Hayyan et al., 2014, Huang et al., 2013), enzyme activation and stabilisation applications (Huang et al., 2014), isomers separation (Hou et al., 2014), supercritical fluids applications (Martins et al., 2014), adsorption applications (Lopez-Salas et al., 2014), alcohol oxidation (Azizi et al., 2014), alcohol ester separation applications (Maugeri et al., 2012), lubricants (Abbott et al., 2014), synthesis applications (Sanap and Shankarling, 2014), fuel desulphurisation (Li et al., 2013) and plastics applications (Leroy et al., 2012).

2.5.8 The Contribution of DESs in the Conversion of Biomass

In addition to the applications mentioned above, DESs are also involved in the reforming of raw biomass to carbohydrates and then to intermediates for a variety of applications. Xia et al. (2014) reported a cellulosic biomass hydrolysis in two different

DES systems composed of ChCl/urea and ChCl/glycerol at a molar mixing ratio of 1:2. Both systems showed competitive hydrolysis rates for cellulose compared to the rates obtained from conventional ionic liquids. The ability of ethylene glycol and ChCl to function as a cheap and low viscosity DES mixture was investigated for the pre-treatment of rice husk as a lignocellulosic biomass source by Gunny et al. (2014). The cellulose showed stability of 90% in the presence of the selected DES. Zhang et al. (2012a) investigated the ability of an inexpensive and green mixture of choline derived for cellulose recrystallisation. The results obtained revealed that 6 wt% of cellulose dissolved at 110 °C after 10 min. Glucose isomerisation followed by fructose dehydration to 5HMF was carried out in a DES mixture composed of ChCl/glucose and catalysed by mineral acids in a biphasic system of MIBK/water. At the optimum conditions, 70% of 5HMF yield was obtained (Liu et al., 2013). The same group also reported that no reaction occurred when they tried to convert glucose to 5HMF in a ChCl/glucose DES at 180 °C and catalysed by $Cu(NTf)_2$. This was attributed to the loss of reactivity of glucose due to its stabilisation caused by hydrogen bond interaction with ChCl.

The pre-treatment of biomass aims to produce carbohydrates, which are the dominant feedstock of a variety of chemicals and fuels. Carbohydrates are traditionally produced from biomass using different systems, all of which suffer from many drawbacks. In order to overcome these drawbacks and due to the advantages of DESs, such as the ability of composing DES mixtures from carbohydrates and ChCl as shown in Table 2.14, great interest has been shown in using DES mixtures in the conversion of carbohydrates to furans (Vigier et al., 2015). Different types of carbohydrates have been converted to the platform compound 5HMF in DES, using different approaches. Ilgen et al. (2009) reported a 30% yield of 5HMF from fructose dehydration catalysed by Lewis acids in a DES mixture of ChCl/urea at 100 °C. The low yield of 5HMF obtained from this reaction

was attributed to the activation of side reactions between the substrate fructose and urea. Hu et al. (2008) reported a 5HMF yield of 66% for the dehydration of fructose to 5HMF at a reaction time of 60 min and reaction temperature of 80 °C, using a biphasic system, AcOEt as an extraction solvent and a DES of ChCl/Citric acid.

Table 2.14. Different DESs made from ChCl and carbohydrates and their freezing points (Vigier et al., 2012)

No.	DES	Molar ratio	Freezing point °C
1	ChCl/glucose	1:1	80
2	ChCl/fructose	3:2	70
3	ChCl/inulin	3:2	80
4	ChCl/sucrose	1:1	80
5	ChCl/sorbitol	1:1	RT
6	ChCl/xylitol	1:1	RT
7	ChCl/glycerol	1:2	RT

RT: Room Temperature

Vigier et al. (2012) reported a 5HMF yield of 80% for the fructose dehydration to 5HMF in a DES composed of ChCl, water and Betaine hydrochloride (BHC) as an ionic carboxylic acid at a molar ratio of (10:2:0.5) and reaction temperature of 150 °C. In another publication, where BHC acid in aqueous solution was reported as a catalyst to convert xylan to furfural, approximately 70% was obtained at 150 °C (Liu et al., 2014).

2.5.9 Production of 5HMF from Biomass in Deep Eutectic Solvents

Fructose was dehydrated in different DESs such as ChCl/oxalic acid, ChCl /malonic acid and ChCl /citric acid, involving ethyl acetate as an extraction solvent (Hu et al., 2008). The highest 5HMF selectivity of 83.3% was obtained with conversion of 91.9% when a DES composed of ChCl /citric acid was used at 80 °C and 60 min of reaction time.

Also in this study, it was found that the use of the extraction solvent increased the 5HMF yield by 9% compared to runs conducted in a monophasic system without adding ethyl acetate (Hu et al., 2008). This may be attributed to the efficient role of the ethyl acetate as an extraction solvent in the separation of the reactive phase from the organic phase, which suppresses the rehydration of 5HMF to levulinic and formic acids. The same authors reported that inulin was converted to 5HMF using two DES systems composed of ChCl /oxalic acid and ChCl /citric acid in a biphasic system composed of ethyl acetate. 5HMF yields of 64% and 55%, respectively, were obtained from the above mentioned systems (Hu et al., 2009). Both experimental results reported by the same authors were obtained using different substrates and DESs composed of different carboxylic acids. This indicates that the composition of the DES and the type of the substrate greatly affect the conversion reactions of biomass to 5HMF in DES media.

In another study, 20% fructose solution was dehydrated in ChCl to 5HMF at 120 °C in a system pressurised by 4MPa of CO_2. This reaction was catalysed by in-situ carbonic acid, obtained from the CO_2 reaction with water generated from fructose in the reaction. At the end of the reaction, CO_2 was depressurised and 5HMF was extracted by MIBK using the fact that ChCl has low solubility in MIBK. The highest yield of 5HMF obtained was 74% after 90 min (Liu et al., 2012). However, this system was limited by the use of water to dissolve the fructose, which could lead to 5HMF rehydration. Furthermore, the use of CO_2 made the process not green, unlike the DES systems described in this thesis where an open system was used. Low melting point mixtures consisting of different hydrocarbons and ChCl were studied for the conversion of carbohydrates to 5HMF using different acid catalysts (Ilgen et al., 2009). A DES mixture composed of fructose and ChCl at a mass ratio of 4:6 and catalysed by p-TSA was found to give the best carbohydrates conversion to 5HMF. The optimum results obtained are listed in Table

2.15. In this thesis, the p-TSA was used as an HBD and catalyst at the same time, and a higher 5HMF yield was obtained (Assanosi et al., 2014, Assanosi et al., 2016).

Table 2.15. Conversion of carbohydrates to 5HMF in a DES composed of fructose and ChCl (Ilgen et al., 2009)

Substrate	Catalyst	Time (min)	Temp. (°C)	5HMF yield %
Fructose	pTsOH	30	100	67
Glucose	$CrCl_2$	60	110	45
Sucrose	$CrCl_2$	60	100	42
Inulin	pTsOH	60	90	57

Different publications have reported the dehydration of different carbohydrates to 5HMF in DES systems. These systems use an external catalyst and/or solvent as reaction media, as listed in Table 2.16, thus adding additional cost to any future scaled up process. For example, Zhao et al. (2014) dehydrated fructose to 5HMF in a DES. Compared to the DES systems investigated in this thesis, although this system requires a shorter reaction time and produces a high 5HMF yield, it also requires an external catalyst and higher reaction temperature. A DES composed of citric acid and ChCl was used to study the stability of 5HMF in organic liquids. The study concluded that the 5HMF yield of 66% was stable at a reaction temperature below 80 °C (Kobayashi et al., 2015). Liu et al. (2013) investigated the use of ChCl as an additive to enhance the selectivity of chloride metal catalysts for one pot glucose isomerisation and dehydration to 5HMF in a biphasic system of water and MIBK. This study has limitations such as the relatively low 5HMF yield, negative ecological effects and the possibility of 5HMF rehydration due to the use of water and MIBK as a reaction medium. A combination of quaternary ammonium salt (TBAB) and $SnCl_4$ was used to catalyse glucose conversion to 5HMF in the presence of

the DMSO as a solvent (Tian et al., 2013). Despite the catalytic activity of DMSO and the relatively high reaction conditions, the yield obtained was not promising. In contrast, Matsumiya and Hara (2015) reported a lower yield at higher reaction conditions for the glucose conversion to 5HMF, catalysed by $B(OH)_3$ in a DES composed of choline dihydrogen citrate and glycolic acid with the addition of a small amount of water as a co-solvent. The low yield was attributed to the low activity of boric acid as a catalyst and the presence of water, which rehydrated the 5HMF. In a kinetic study of lignocellulosic biomass conversion to 5HMF and furfural using a microwave as the heating source, it was found that DES mixtures of ChCl/oxalic acid and ChCl/betaine were the most efficient DES mixtures (Da Silva Lacerda et al., 2015). This study was conducted in sulfolane and water as co-solvents and TiO_2 as a catalyst in the time and temperature ranges of 5 to 60 min and 120 to 200 °C, respectively. A total yield of furfural and 5HMF of 53.24% was obtained. Xylose and xylan were converted to furfural using a DES composed of ChCl and oxalic acid with MIBK. Furfural yields of 60.4 and 55.5% were obtained, respectively (Zhang et al., 2014).

Fructose was dehydrated to 5HMF and catalysed by p-TSA at a reaction temperature of 80 °C and long reaction time of 1920 min in an ionic liquid $[BMIM]BF_4$ with DMSO as a co-solvent for the solubilisation of fructose. A 5HMF yield of 68% was achieved (Lansalot-Matras and Moreau, 2003). This clearly shows the efficiency of the DES of ChCl and p-TSA used in this thesis. In the dehydration of fructose to 5HMF in methanol and THF as the reaction medium, ChCl was used for the impregnation of $AlCl_3/SiO_2$ as a solid catalyst to facilitate a good contact between the insoluble carbohydrates and solid catalyst by forming an in-situ DES between ChCl and the carbohydrates (Yang et al., 2015). However, the reported yield was still relatively low. Zakrzewska et al. (2011) reported that due to the high polarity of the ChCl/fructose DES mixture, it has poor

miscibility with both low boiling point organic solvents such as ethyl acetate (34 °C) and high boiling point organic solvents such as MIBK (117 °C). This phenomenon could lead to a better 5HMF yield in fructose dehydration in this DES by performing an efficient continuous extraction of 5HMF in organic phase, and therefore eliminating the rehydration of 5HMF to levulinic and formic acid.

Table 2.16. Previous studies of carbohydrates' conversion to 5HMF in different DES systems

Substrate	DES	Solvent	Catalyst	Temp. (°C)	Time (min)	Conv. %	Sel. %	Yield %	Ref.
Fructose	ChCl/fructose	Ethyl acetate	(HPAs)	110	1	93.3	83.3	92.3	(Zhao et al., 2014)
Fructose	ChCl/citric acid with [Bmim]Cl	Ethyl acetate	-	80	-	-	-	66	(Kobayashi et al., 2015)
Glucose	ChCl	Water/MIBK	Chloride metal	-	-	-	-	70	(Liu et al., 2013)
Glucose	TBAB	DMSO	$SnCl_4$	100	120	-	-	69.1	(Tian et al., 2013)
Glucose	Choline dihydrogen citrate/glycolic acid	Water	$B(OH)_3$	140	240	-	-	60	(Matsumiya and Hara, 2015)
Fructose	ChCl	Methanol and THF	$AlCl_3/SiO_2$	120	80	-	-	58	(Yang et al., 2015)

2.6 Fructose Dehydration Reaction Kinetics

There have been few kinetic studies on the dehydration reaction of fructose to 5HMF reported in the literature. Table 2.17 shows the reaction order reported in the literature for this dehydration reaction using different catalysts and solvents. It is clear that most of the reactions reported followed first-order reaction kinetics. Kobayashi et al. (2015) modelled fructose conversion to 5HMF as parallel and consecutive reactions using a biphasic system with DES (citric acid and ChCl) and/or [Bmim]Cl as the catalyst and ethyl acetate as the solvent at 70 – 120 °C. They found that the fructose conversion followed first-order kinetics for low initial fructose concentrations (≤ 10% (kg/kg of IL)) and observed a deviation when the initial fructose concentration was greater than 20% at 70 °C. The formation of 5HMF followed a consecutive path in the order of fructose to intermediate to 5HMF (Kobayashi et al., 2015); hence, the activation energy reported in Table 2.17 is that for intermediate to 5HMF (110 kJ/mol).

Table 2.17. Kinetics of fructose dehydration reactions for different catalysts and solvents

Catalyst	Solvent	Temp. range (°C)	Time range (min)	Reaction order	Activation Energy (kJ. mol^{-1})	Preexponential factor (A)	Ref.
Sulphonic acid	DMSO	100-140	6-60	1st	55	8.95×10^{7} h^{-1}	(Chen et al., 2014)
Heteropolyacid	[BMIM]Cl	60-80	0-5	1st	31.88	2.38 min^{-1}	(Xiao and Song, 2014)
Brønsted acidic ionic liquid	Isopropanol	90-110	0-180	1st	62.1	5.7×10^{7} min^{-1}	(Ma et al., 2015)
Zirconium phosphate	DMSO	60-120	30-150	1st	52	-	(Xu et al., 2015a)
ChCl/citric acid	Ethyl acetate	70-120	0-240	1st	110	-	(Kobayashi et al., 2015)
A mixture of sulphonic acid, ionic liquid and silica	DMSO	90-140	0-180	1st	67.5	-	(Lee and Wu, 2012)
Heteropolyacid	DMSO	80-160	0-350	1st	27.21	11.72 min^{-1}	(Song et al., 2016)

2.7 Conclusions

From the literature reviewed, it was found that 5HMF is an important feedstock to produce valued chemicals, bioplastics, and biofuels such as DMF, which is viewed as a substitute for petrol.

5HMF can be produced from a variety of biomass such as carbohydrates like glucose and fructose using different acid catalysed and non-catalysed systems such as aqueous systems, organic solvents, and ionic liquids.

Fructose, however, was reported as the optimum feedstock among the different carbohydrates. This is because of its ability to be readily dehydrated to 5HMF compared to other carbohydrates such as glucose, which requires an isomerisation step prior to the dehydration reaction.

It was also discovered that the use of aqueous systems (composed of mineral acids as catalyst and water as solvent) for the dehydration of fructose to 5HMF required high temperatures and pressures, and produced only low yields of 5HMF. In addition, these systems would involve high operational costs and would lead to a negative ecological and environmental impact from the generated waste. These drawbacks impede the commercialisation of 5HMF production. In this study, a dual function material (DES) is developed to serve as catalyst and solvent in the dehydration of fructose to 5HMF. Three different DES systems were formulated using cheap and renewable materials, which would reduce the cost associated with the use of aqueous systems. The DES mixtures can be readily prepared compared to the heterogeneous catalysts reported in the literature. The dehydration reactions of fructose to 5HMF using the different DES systems were carried out at mild reaction temperatures and atmospheric pressure, which would also reduce the operational costs incurred compared to using aqueous systems, ionic liquids, or heterogeneous catalysts. Unlike aqueous systems (mineral acids and water), the DES

system produces high yields of 5HMF, since the rehydration of 5HMF caused by the presence of water has been eliminated. Each formulated DES is composed of acid and salt, where the acid is the HBD and acts as a catalyst, while the DES is the reaction medium. This eliminates the need for an external catalyst and solvent, and hence is referred to as a self-catalysed system.

Chapter 3 Experimental Setup, Materials and Methods

3.1 Overview

This chapter outlines the materials used in this work and their specifications and suppliers. The experimental procedure, the setup of experiments and equipment used are also described in this chapter, in addition to the analytical method and procedure.

3.2 Materials

The commercial chemicals and materials used in this work are listed in Table 3.1. All the chemicals were used as received from the supplier without further purification, unless otherwise stated.

Table 3.1. Commercial chemicals and materials used in this study

Item	Specifications	Supplier
p-Toluenesulfonic acid monohydrate (p-TSA)	**98.5% (d**ual catalyst and HBD)	Sigma-Aldrich
Adipic acid	99% **(d**ual catalyst and HBD)	Sigma-Aldrich
Choline chloride	**99% (organic salt)**	Acros Organics
N,N-Diethylethanolammonium chloride	**≥98% (organic salt)**	VWR
D-Fructose	**99% (reactant)**	Sigma-Aldrich
Water HiPerSolv CHROMANORM for HPLC	**HPLC mobile phase**	VWR
Calcium hydroxide	96% pH modifier	Sigma-Aldrich
5-Hydroxymethylfurfural ≥	99% HPLC analytical standard	Sigma-Aldrich
Heating oil	Reaction heating medium (Boiling point: 415 °C)	Acros Organics

3.3 Methodology

3.3.1 Experimental Plan

An experimental plan could be either: (1) Design of Experiment (DOE), where several factors can be investigated in one experiment; or (2) One Factor At a Time (OFAT), where a particular factor is treated while the rest variables are maintained constant. DOE is mostly used to establish the relationship between variables that influence a process and its output. The information obtained is used for optimisation, modelling and screening of the process variables. This approach is rigorous, takes time to develop and involves statistics (Cox and Reid, 2000, Schmitz et al., 2016). The knowledge of statistics is also a prerequisite for its implementation. On the other hand, the OFAT can be used to gain insight into the effect of a given process variable on the process output. The OFAT approach provides rapid information and suboptimal results on the effect of a process variable, while the others are held constant (Schmitz et al., 2016).

The DOE approach is generally more desirable than OFAT because DOE has many advantages. However, with the OFAT approach the full trend and the impact of one process factor can be monitored. As a consequence, the OFAT approach is easy to use compared to the DOE approach (Schmitz et al., 2016). Also, OFAT provides a larger amount of data sufficient to gain process understanding within a short time period (Wu and Hamada, 2011). The experiments can be monitored and more rapidly react to the data than when using DOE (Qu and Wu, 2005). Therefore, in this study the OFAT approach was considered because this project aims to screen the ability of a novel DES to self-catalyse the dehydration reaction of fructose to 5HMF and determine the optimum reaction conditions. The use of the DOE approach requires the use of statistical software package, and this expertise would require time to acquire under the limited timeframe of this study. The experimental conditions used in this study are presented in Table 3.4.

Table 3.2. The ranges of the experimental variables studied in this thesis

Variable	Range
Temperature (°C)	50, 60, 70, 80, 90, 100, 110 and 120
Reaction Time (min)	1 – 180
Feed Mass Ratio ($g.g^{-1}$)	2.5 – 100
DES Molar Mixing Ratio (acid-to-salt)	0.5:1, 1:1, 1.5:1 and 2:1

It is worth mentioning that the experiments were carried out at agitation speeds of 100, 200, 300, and 400 rpm to study the effect of mixing. It was observed that at 100 and 200 rpm little or no reaction occurred, as revealed by the analysis for the presence of 5HMF. When the experiment was carried out at 400 rpm, however, there was splashing of the reaction medium on the reactor walls, thus reducing the amount of material available for reaction. Therefore, the best agitation speed that resulted in significant reaction without loss of the reaction medium was 300 rpm. Hence, the experiments reported in this study were carried out at 300 rpm. Note also that the reaction time starts when the temperature of the reactor medium is approximately (± 0.5°C) that of the oil bath.

3.3.2 Experimental Setup

To investigate the effect of different reaction parameters on fructose dehydration to 5HMF in DES, an open batch system was used in a fume cupboard. As illustrated in Figure 3.1, it consisted of either a 100 ml glass or a stainless steel beaker as the main reactor, which was placed in a 500 ml oil bath as the heating medium. The oil bath was heated by a controllable electrical magnetic stirrer hot plate. The DES and reaction mixtures, as well as the heating oil, were stirred by magnetic bars at 300 rpm.

3.4 Equipment

3.4.1 IKA Magnetic Stirrer Hot Plate

The magnetic stirrer hot plate used (Model No. 01.672700 from IKA, Germany) is illustrated in Figure 3.1. It has a heating capacity range from 0 to 340 °C, and a stirring range from 0 to 1500 rpm. The temperature is controlled by two thermocouples placed in the oil bath.

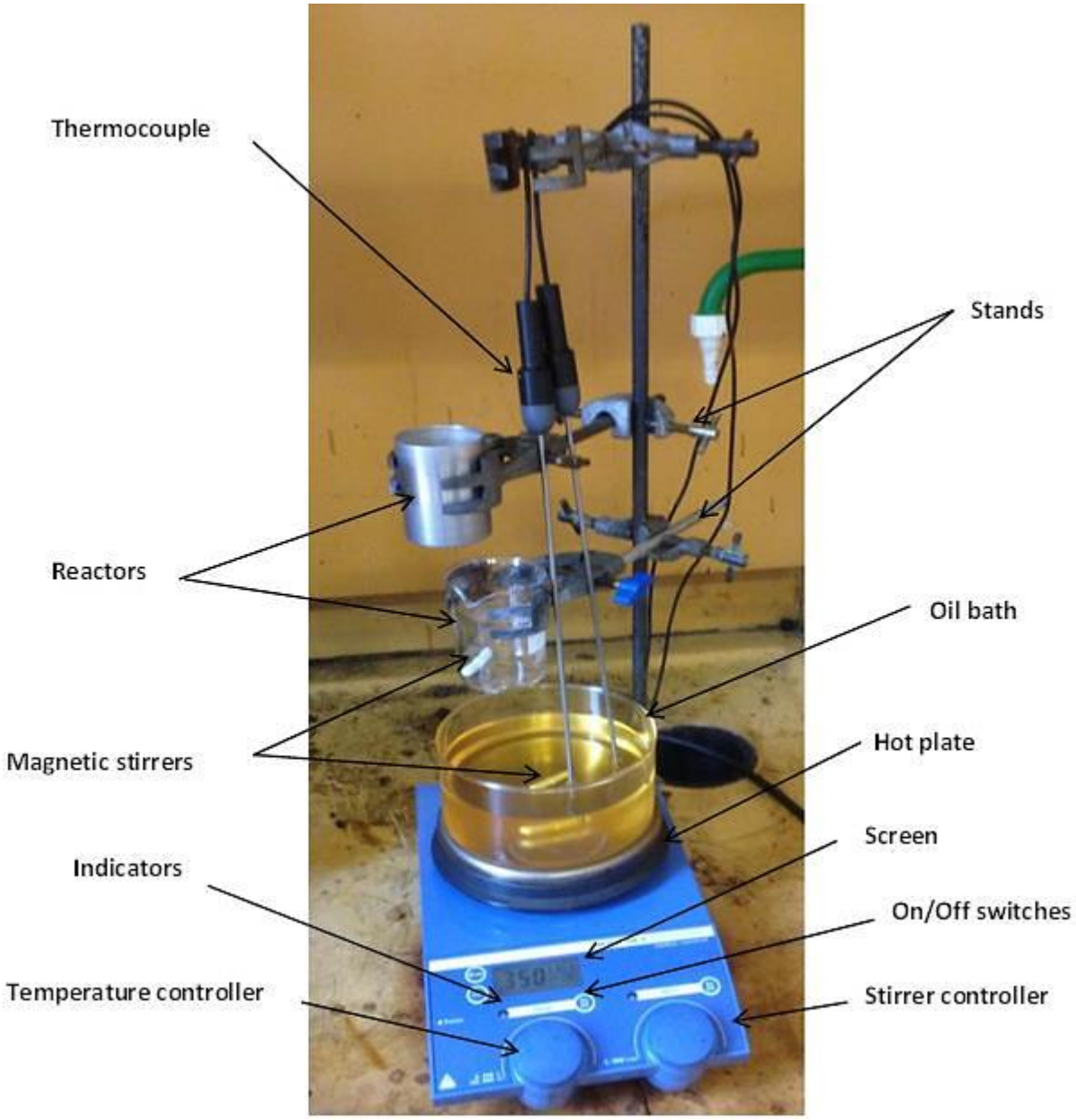


Figure 3.1. Open system used for fructose dehydration reactions (agitation speed of 300 rpm)

3.4.2 Oil Bath

The oil bath (Scientific Glass Laboratory, UK) used was a 500 mL round glass vessel with a diameter of 130 mm, as shown in Figure 3.1.

3.4.3 Main Reactor

Beakers made of glass and stainless steel and of 100 mL capacity were used as reaction vessels.

3.4.4 Balance

A balance (Model No. AR2140, from Ohaus Adventurer Balances, Switzerland) was used to weigh the materials. It has a weighing capacity of 210 g, readability of 0.1 mg, and is regularly calibrated by Precision Balance Services.

3.4.5 pH Meter

A SevenMulti pH meter (Metter Toledo, UK) was used to measure the pH of the sample prior to analysis by HPLC. It has a pH in the a temperature range from -30.00 to 130 °C. It is provided with an electrode and an electrode holder and LCD display. It was always calibrated before measuring the sample with three different calibration buffers with pH values of 4, 7 and 10.

3.4.6 Vacuum Oven

A GallenKamp vacuum oven (Fistreem International Ltd, UK) was used to dry the chemicals prior to use. It was connected to a vacuum pump, equipped with a thermostat and safety controller, and operates within the temperature range from 0 to 200 °C.

3.4.7 Syringe Filters and HPLC Vials

Twenty-five millimetre syringe filters with pore size of 0.2 μm GHP membrane made of polyethylene were used to filter the sample prior to pouring it into HPLC vials. The filters were connected to 10 mL plastic syringes. HPLC glass vials (Agilent Technologies, UK) 2 mL in volume were used to store the samples for HPLC analysis.

3.4.8 Rotamixer

A rotamixer (Hook and Tucker Instruments, UK) was used to shake the samples well for mixing prior to analysis.

3.4.9 Ultrasonic Bath

An ultrasonic bath (Grant Instruments Ltd, UK) was used to sonicate the mobile phase to expel air bubbles prior to the sample passing through the HPLC.

3.4.10 Experimental Procedure

The calculations for determining the mole ratios of the DES mixtures and the feed ratios of fructose are detailed in Appendices B and C, respectively. The calculations of the 5HMF yield, selectivity and fructose conversion equations and procedures are detailed in Appendices A and D.

3.5 Preparation of Deep Eutectic Solvents and Fructose for the Dehydration Reaction to 5HMF

Three different DES solvents were prepared for the dehydration of fructose to 5HMF. These were made in different molar ratios between the acid and the salt (composing the DES) to study the effect of the molar mixing ratios on the dehydration reaction of fructose to 5HMF. Prior to mixing the salt and acid, both materials were dried separately at 70 °C under vacuum for 120 min. This step was carried out to remove moisture from the materials for two main reasons: (1) to make the materials easy to handle on the balance, and (2) to exclude the moisture mass from the calculated mass of the material for the DES preparation.

An equivalent mass to the required molar ratio of each material was then weighed and mixed together in a 100 mL glass beaker covered by foil. The contents of the beaker

were agitated by a magnetic stirrer bar at 300 rpm and heated at 80 °C in an oil bath in a fume cupboard for 30 min, where the mixture became a homogenous liquid. Then, the oil bath temperature was adjusted to the desirable dehydration reaction temperature, and the weighed mass of fructose was added to the reaction beaker, which was again covered with foil. The reaction mixture was then stirred and heated in the fume cupboard for a known reaction time. The reaction beaker was then taken out from the oil bath and immediately placed in an ice bath to stop the reaction by lowering the temperature to 0 °C. When the mixture was cooled down a frozen brown mixture was obtained. Afterwards, the mixture was dissolved in 5 ml HPLC grade water by agitating it with a glass rod.

3.5.1 Analysis of Reaction Samples

Experimental samples were analysed by HPLC. The main focus in the analysis was quantifying the residual reactant fructose and the desirable product 5HMF. After the samples were dissolved in 5 ml HPLC grade water, the pH was adjusted to 7 by using a base modifier of 2 M calcium hydroxide solution. Then, using a 250 mL pipette, the sample volume was adjusted to 100 ml as a total volume for analysis. Afterwards, the sample was poured into a 250 mL glass bottle and shaken. Then, a part of it was filtered using a 0.2 μm syringe filter and approximately 1.5 mL was bottled in a 2 mL HPLC vial for HPLC analysis.

3.5.2 High-Pressure Liquid Chromatography

Both the initial reactant fructose and the final product 5HMF were analysed by HPLC 1100 Agilent series, using a refractive index (RI) detector as shown in Figure 3.2, and a Rezex RCM-monosaccharide column.

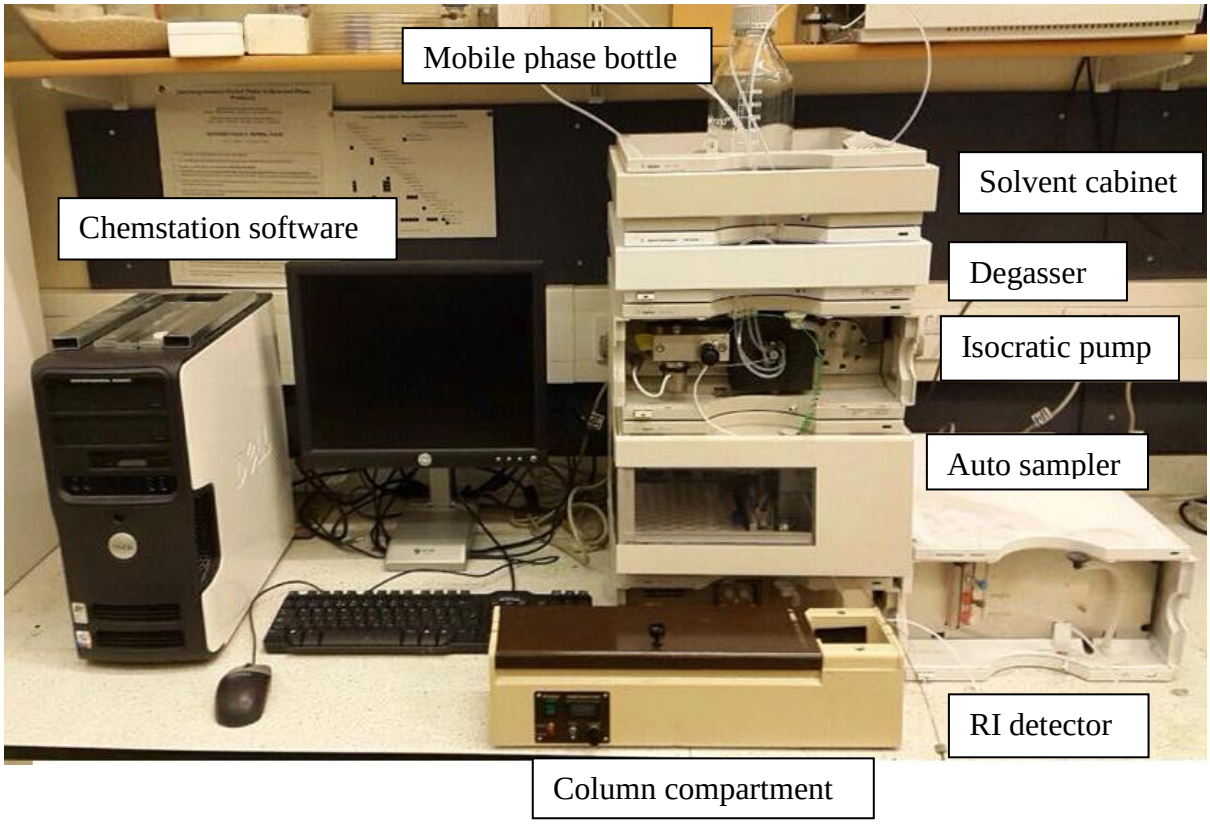


Figure 3.2. HPLC 1100 Agilent series

3.5.3 Refractive Index Detector

The RI detector illustrated in Figure 3.2 is the main part of the HPLC, where every single component is detected individually after separation in the column. In this work, an Agilent 1200 series refractive index detector (Serial No. CN60555933) was used. It has a refractive index range of 1.00 to 1.75 refractive index unit (RIU), measurement range of ± 600×10^{-6} RIU, sample cell volume of 8 µl, maximum pressure of 5 bar, maximum flow rate of 5 ml/min and sample pH range of 2.3 to 9.5. It was chosen as the sugars cannot be detected by any other type of HPLC detector such as a diode array detector (DAD) or a variable wavelength detector (VWD). Most importantly, the RI detector also has the capability of detecting the final product, 5HMF.

3.5.4 The HPLC Column

The column used in this work, an RCM-Monosaccharide (Part No. 00H-0130-KO), was equipped with a column guard (Part No. 03B-0130-KO) and supplied by Phenomenex, UK. It has dimensions of 300 × 7.8 mm. It has a calcium-based stationary phase with particle size of 8 μm and maximum operating pressure of 69 bar, with a maximum flow rate of 1.0 ml/ min and maximum temperature of 85 °C. The recommended mobile phase storage solvent is water at neutral pH. The cleaning procedure is 100% water at a flow rate of 0.4 mL/min and a temperature of 85 °C for at least 720 min. For the column regeneration, 0.1 M $Ca(NO_2)_2$ solution was used as the regeneration solvent at a flow rate of 0.2 ml/min and a temperature of 85 °C in a time range of 240 to 960 min.

3.5.5 HPLC Method

The HPLC method used for analysing the feed materials and the final product consists of HPLC grade water as the mobile phase with a maximum flow rate of 5 ml/min, sample injection volume of 20 μl, analysis method time of 40 min, column oven temperature of 75 °C and RI detector temperature of 40 °C. Known concentrations of standard samples of fructose and 5HMF were first injected into the HPLC to determine the retention time of both materials, as shown in Figure 3.10 and Figure 3.11. Calculations of the calibration curves are illustrated in Appendix E.

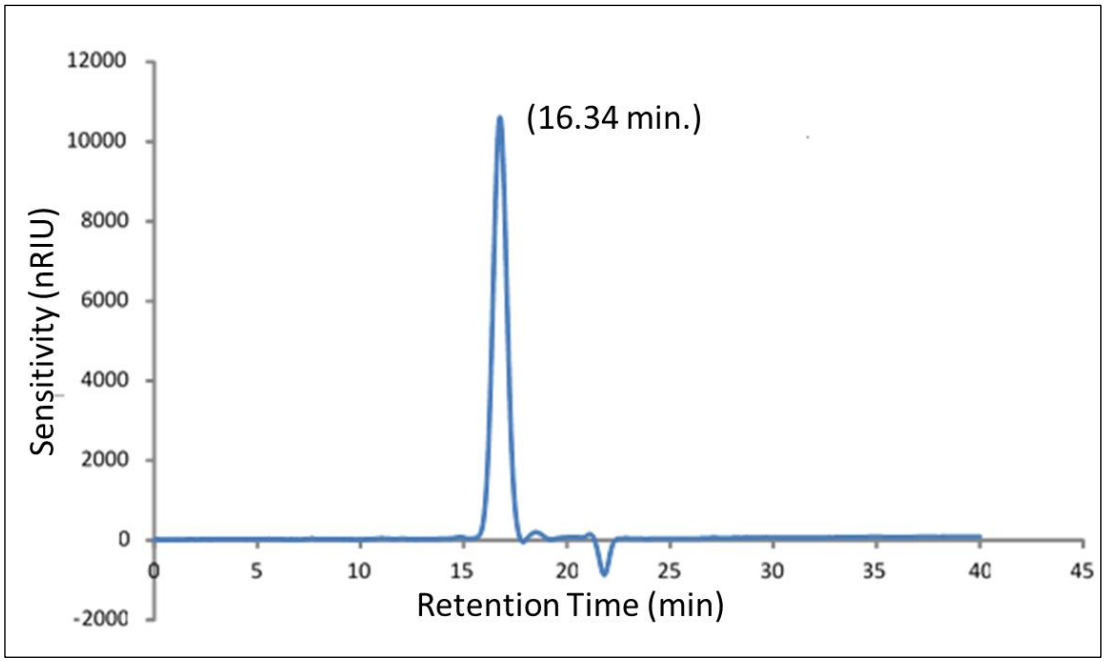


Figure 3.3. Standard fructose retention time

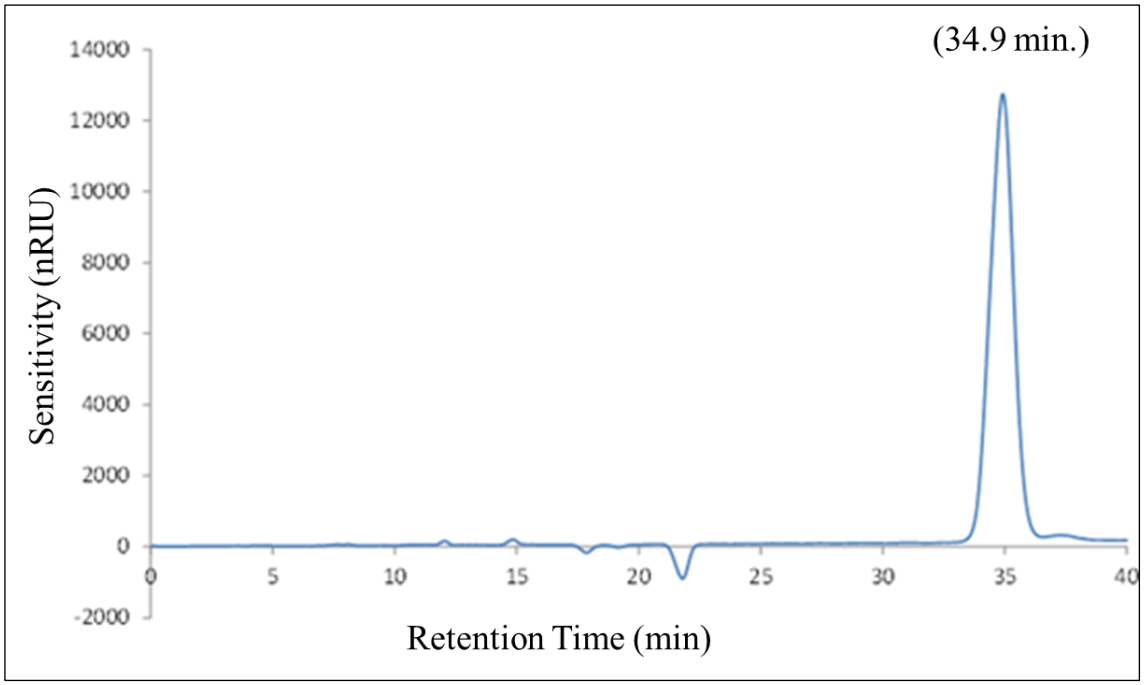


Figure 3.4. Standard 5HMF retention time

Chapter 4 Facile Acidic p-TSA-Choline Chloride DES-Catalysed Dehydration of Fructose to 5-Hydroxymethylfurfural

4.1 Abstract

The conversion of lignocellulosic biomass to biofuel precursors such as 5HMF and levulinic acid has recently been the focus of intensive research due to the supplementary role of biofuels as future transportation fuels. 5HMF is a molecule from which high-value chemicals and biofuel molecules such as 2,5-Dimethylfuran (DMF) can be produced. In this chapter, an environmentally friendly Brønsted acidic Deep Eutectic Solvent (DES) (consisting of p-toluene sulfonic acid monohydrate (p-TSA) ($C_7H_8O_3S$) and choline chloride salt (ChCl) ($C_5H_{14}ClNO$) was used for the dehydration of fructose to 5HMF. This DES (p-TSA–ChCl) plays a dual role as both a hydrogen bond donor (HBD) and as a catalyst for the promotion of the dehydration reaction, thus obviating the need for an external acid. The reaction was carried out in a batch system, at temperature ranges of 50 – 110 °C, time 5 – 120 min, feed ratio (fructose-to-DES) ($g.g^{-1}$) 2.5 – 100, DES molar mixing ratio 0.5 – 2, (acid-to-salt) and stirring speed 300 rpm at atmospheric pressure (1 atm). It was found that fructose was readily dehydrated to 5HMF. The optimum reaction conditions, giving the highest 5HMF yield of 78.3%, were at a temperature of 80 °C, a DES molar mixing ratio of 1.5:1 (p-TSA to ChCl), with a feed ratio of 5, a reaction time of 60 min at agitation speed of 300 rpm and pressure 1 atm.

4.2 Introduction

As mentioned in section 2.4 (Chapter Two), the dehydration of fructose to 5HMF was investigated in different systems, where their drawbacks and limitations were debated. The fructose dehydration reaction mechanism and its possible side reactions are illustrated in Figure 4.1.

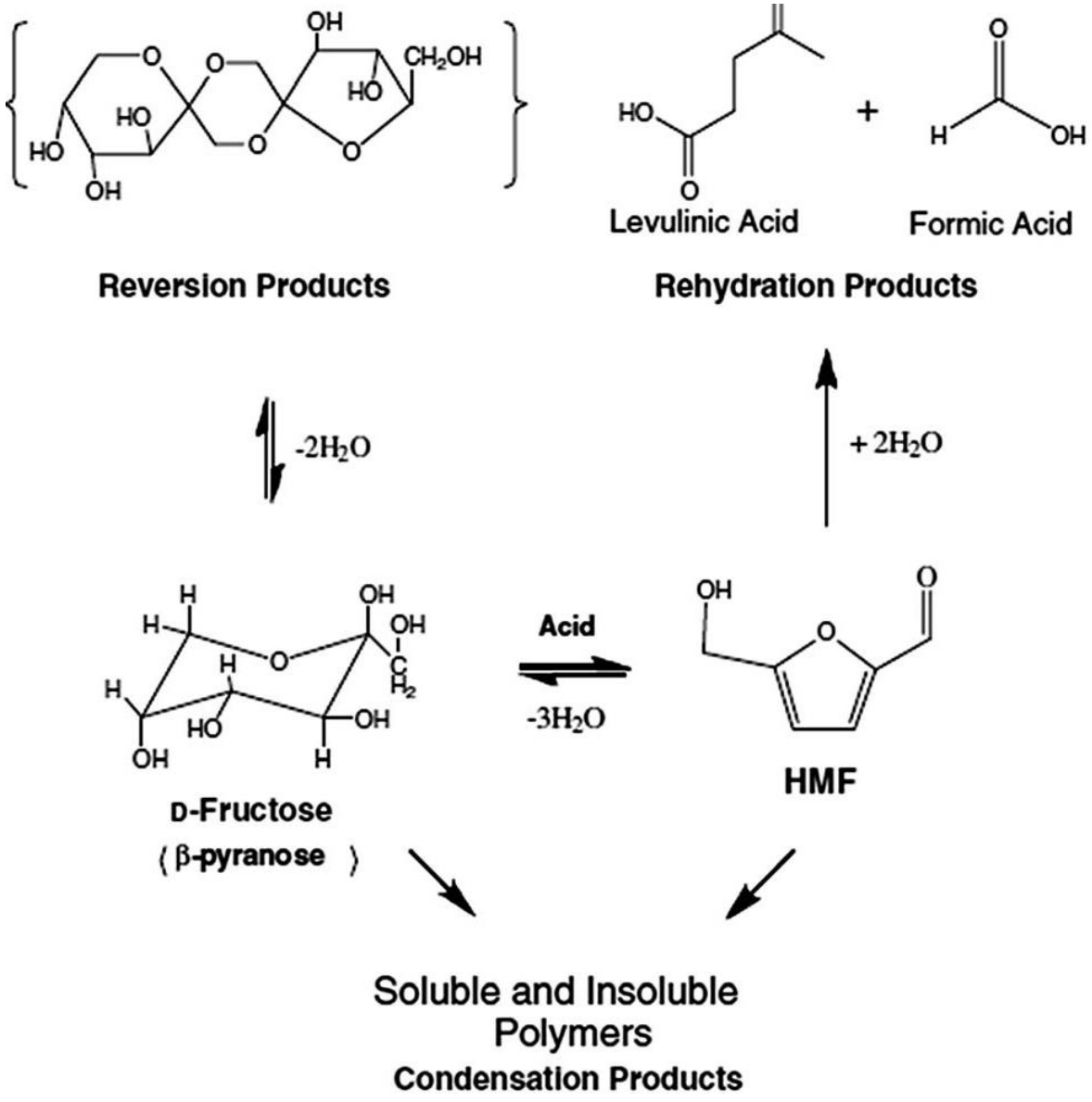


Figure 4.1. The schematic diagram of catalysed fructose dehydration reaction and the possible sub reaction pathways (Roman-Leshkov and Dumesic, 2009)

In all the previously mentioned systems for the dehydration of fructose to 5HMF, the addition of an acid catalyst is required, which is generally undesirable from a processing viewpoint because of corrosion and the fact that its waste is not environmentally friendly.

In this study, the self-catalysed dehydration of fructose to 5HMF using an acidic DES derived from p-toluene sulfonic acid monohydrate (p-TSA) and choline chloride

(ChCl) was investigated. Some of the advantages of using DES are a) it is cost effective and easy to prepare, b) it allows mild reaction conditions compared to the aqueous system reported in the literature, c) it eliminates rehydration of 5HMF as no water is involved in the reaction, and d) it eliminates the need for an external catalyst as p-TSA serves as both HBD and acid catalyst for the dehydration reaction. The DES mixture had no contamination effect as it is not reactive. The effect of different reaction parameters on the dehydration reaction was studied, namely, the effect of the feed ratio, reaction time, reaction temperature and the DES mixing ratios.

4.3 Results and Discussion

The reactions were carried out in an open system for two main reasons: (1)because of the reaction medium used being non-volatile, so enabling the reaction to be done at atmospheric pressure. (2)because it is easier with an open system to add the reactant and count time zero when the desirable temperature is reached, and the DES is well mixed.

In addition, due to the high viscosity of the DES, it was easier at the end of the reaction to recover the whole reaction sample in an open system compared to in a closed system. Throughout the experimental work, the experiments were conducted three times; the calculated using Equations (A-1), (A-2) and (A-3) (see Appendix A). It is important to mention here that it was not possible to use organic solvents for extraction to investigate the reusability of the DES systems used in this work, this because of the HPLC column used for analysing the experimental samples could only accept water as a solvent. Thus, reusability studies are recommended as future work. The standard deviation was used to quantify the variation within the experimental resultsof the5HMF yield, selectivity and fructose conversion.

4.3.1 The Effect of Feed Ratio

The feed mass ratio is defined as the ratio of the fructose mass to the total DES mass used (see Appendix A, Equation A-4). The effect of the feed ratio on fructose conversion, 5HMF yield and selectivity was investigated at a reaction temperature of 80 °C, reaction time of 60 min, a DES molar mixing ratio of 1:1 (acid-to-salt) and agitation speed of 300 rpm. These conditions were chosen as they showed a good 5HMF yield based on the initial results from the experimental plan investigation prior to the start of the experimental work. The study of the feed ratio effect was carried out in a ratio range from 2.5 to 100. Figure 4.2 shows the effect of the feed ratio (i.e. fructose-to-DES ($g.g^{-1}$)) on the fructose conversion, 5HMF yield and selectivity. It is worth noting that four major experiments were initially conducted in triplicate and the average values and standard deviations (i.e. error bars) plotted. However, to obtain a good fit curve, additional experiments were conducted singly at the same conditions, which can be noticed in Figure 4.2.

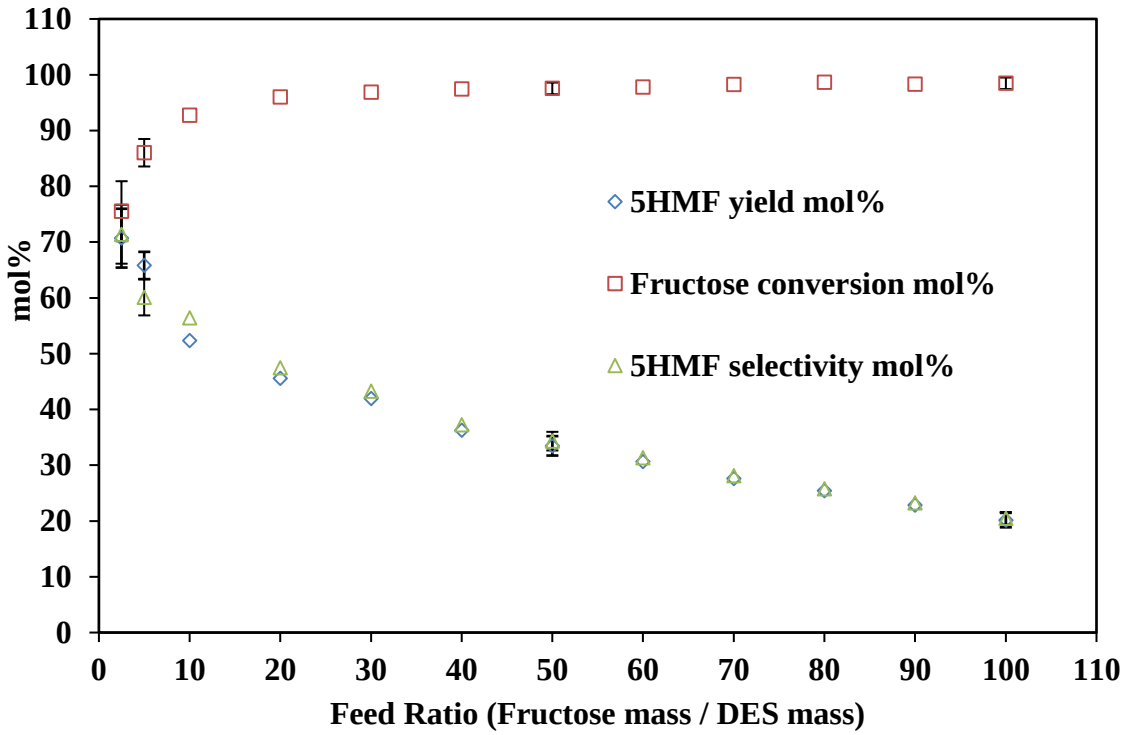


Figure 4.2. The effect of feed ratio on fructose conversion, 5HMF yield and selectivity at reaction temperature 80 °C, time 60 min, agitation speed 300 rpm, and DES mixing ratio of 1:1 (acid-to-salt) at atmospheric pressure.

From Figure 4.2, it can be seen that at feed ratios between 2.5 and 10 the conversion of fructose increased rapidly from 75.5 to 92.7%. As the feed ratio was further increased towards 100, the fructose conversion increased only slightly, especially between a feed ratio of 30 (96.9%) and 100 (98.5%).

As shown in Figure 4.2, the 5HMF yield decreased as the feed ratio (fructose to DES mass ratio) increased. This may be attributed to 5HMF being rehydrated by the presence of water produced from the dehydration reaction of the fructose. The highest yield obtained was 70.7%, with a feed ratio of 2.5, after which the yield sharply decreased to 52.3% at a feed ratio of 10. As the feed ratio increased from 20 to 100, the 5HMF yield

decreased gradually. The lowest yield was 20.5% at a feed ratio of 100. This can be attributed to the fact that increasing the initial fructose concentration (feed ratio) could result in subsequently high 5HMF concentration, which then leads to the occurrence of unwanted side reactions (Ilgen et al., 2009). It has been reported that these reactions produce insoluble humins and/or soluble polymers (Sievers et al., 2009), which lead to a decrease in 5HMF yield. This was noticed from the change of the sample colour to a darker brown as the fructose mass increased. This observed colour change could be an indication of undesirable by-products in the dehydration reaction; however, further analysis was not carried out for confirmation. Due to some limitations associated with the availability of the analysis techniques, such as NMR and gas chromatography mass spectrometry (GC MS), it was not possible in this work to identify the by-products produced from the dehydration reactions of fructose to 5HMF. Therefore, the products such as humins, polymers, formic acid and levulinic acid from the side reactions were compared withsimilar observations reported in the literature. Also, self-polymerisation of 5HMF and cross-polymerisation between fructose and 5HMF could produce polymers in fructose dehydration reactions (Wang et al., 2011). As shown in Figure 4.2, the effect of the feed ratio on the 5HMF selectivity showed a similar trend to the 5HMF yield. The 5HMF selectivity sharply decreased from 71.4 to 56.4% when the feed ratio was increased from 2.5 to 10. As the feed ratio increased from 20 to 100, the 5HMF selectivity decreased gradually from 47.4 to 20.5%. It was mentioned that the increase of initial fructose concentration would encourage the occurrence of polymerisation reactions, which would decrease the 5HMF selectivity (Van Putten et al., 2013). The highest yield was obtained at a feed ratio of 2.5. Upon analysis, a 2.5 feed ratio gave unreproducible results for fructose conversion, 5HMF yield and selectivity. This may be due to an insufficient

amount of fructose; therefore, a feed ratio of 5 was selected for subsequent experiments. Thus the following parameters investigation was carried out at feed ratio of 5.

The trends observed in the obtained results are in good agreement with the literature. The experimental conditions reported in the literature, however, are more severe, with a temperature of 300 °C and pressure of 200 bar (Bicker et al., 2003). Whereas in this system, a high yield of 5HMF was achieved at the mild reaction temperature of 80 °C and atmospheric pressure (1 bar), meaning a lower energy cost and high-safety system. Yang et al. (2015) found that the polymers were produced as a by-product from the single and cross-polymerisation side reactions, which decreased the 5HMF yield and selectivity from 69 to 48% when the initial fructose concentration was increased from 20 to 100 mg/ml. This was upon fructose dehydration to 5HMF in a biphasic system of water/THF (1:3 v/v) at 140 °C for 15 min. Fan et al. (2011) reported a similar observation for fructose dehydration at initial concentrations of 10, 30 and 50 wt% to 5HMF in a biphasic system composed of water/MIBK. The reaction was catalysed by a heteropoly acid ($Ag_3PW_{12}O_{40}$) as a heterogeneous catalyst at 120 °C and over a reaction time of 60 min. Conversion increased slightly with increasing feed ratio. The same study reported that the 5HMF selectivity decreased from 93.8 to 87.4 wt% when the initial concentration of fructose was changed from 30 to 50 wt%. The reduction in selectivity was attributed to the high concentration of fructose, which leads to an increase in the rate of condensation of 5HMF to polymers; moreover, 14% of levulinic acid was detected within the reaction mixture, which means a 5HMF rehydration reaction was accrued by the presence of water as a solvent.

Qi et al. (2008) investigated the effect of different initial fructose concentrations of 2, 5, 10 and 20 wt% on fructose conversion in a reaction medium of acetone/water (70/30 w/w) at a reaction temperature of 150 °C, a reaction time of 20 min and catalysed by ion

exchange resin. It was found that the increase of initial fructose concentration had a very slight effect on the fructose conversion. This study also revealed that the yield of 5HMF decreased from 73.4 to 54.3 wt%, and the selectivity decreased from 88.3 to 82 wt% when the initial fructose concentration increased from 2 to 20 wt%. This reduction in 5HMF yield and selectivity was attributed to the formation of humins, because of the cross-polymerisation between the fructose and 5HMF. Furthermore, Kuster (1990) reported that the presence of water in the dehydration reaction media leads to an increase in 5HMF yield losses in the form of humins, which can be from 20 to 35% when the initial fructose concentration is increased from 0.25 to 1 M in the fructose solution.

Roman-Leshkov et al. (2006) investigated fructose dehydration in a binary phase composed of water/MIBK and catalysed by hydrochloric acid. The 5HMF yield decreased from 48 to 39 wt%, when the initial concentration of fructose increased from 30 to 50 wt%. In another publication, the same author reported a high 5HMF selectivity of up to 80% by using 30 wt% of initial fructose in an efficient continuous extraction biphasic system involving HCl as a catalyst and different organic solvents and salts as extraction phase (Roman-Leshkov and Dumesic, 2009), thus proving that the reduction in 5HMF selectivity is a result of the presence of water in the reaction medium, which leads to the activation of side reactions in the form of 5HMF rehydration and produces formic and levulinic acids. This clearly shows that the increase in initial fructose concentration in a different reaction medium could lead to different by-products. Li et al. (2010) carried out fructose dehydration in $[C_4mim]Cl$ as an ionic liquid and catalysed by HCl at various initial fructose concentrations of 33, 43, 50 and 67 wt%, resulting in decreasing yields of 5HMF of 82, 76, 67 and 51 wt%, respectively.

4.3.2 The Effect of Reaction Time

The fructose conversion, the 5HMF yield, and selectivity in fructose dehydration reactions at a reaction temperature of 80 °C, agitation speed of 300 rpm, with a feed ratio of 5 and a DES molar mixing ratio of 1:1 (acid-to-salt) as a function of reaction time are presented in Figure 4.3. These conditions were chosen from preliminary experiments and the results are described in section 4.3.1, while 300 rpm is moderate for an open system, giving reasonable 5HMF yields.

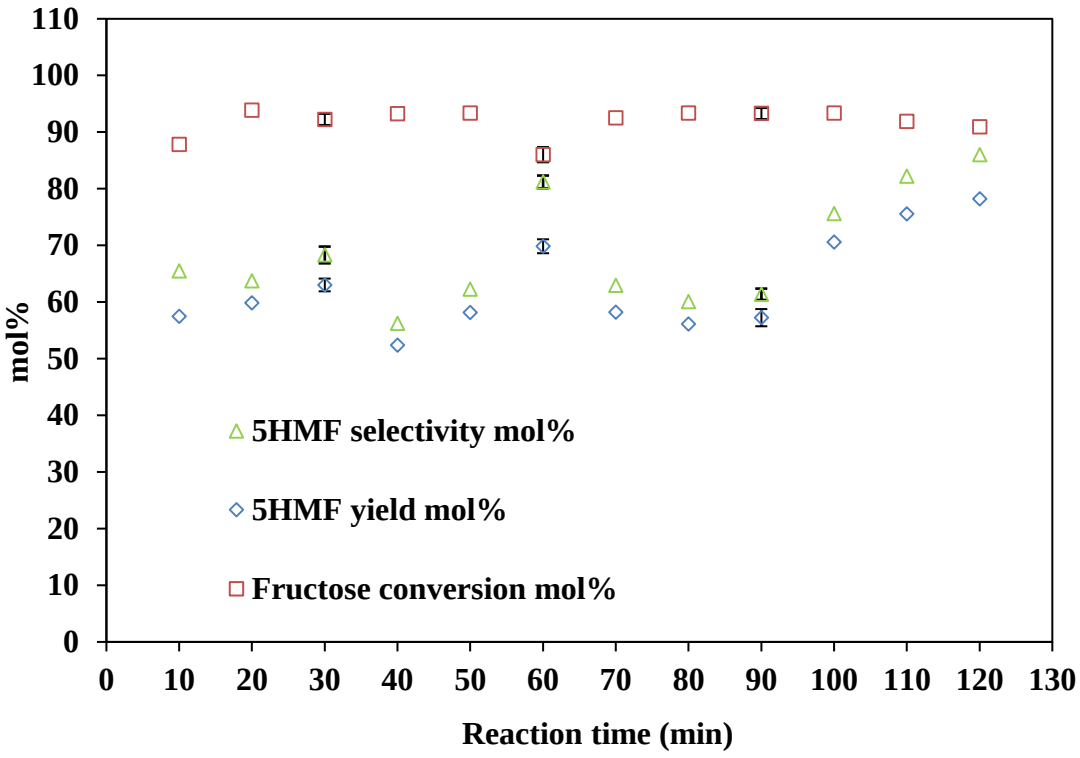


Figure 4.3. The effect of reaction time on fructose conversion, 5HMF yield and selectivity at 80 °C, agitation speed of 300 rpm, with a feed ratio of 5 and DES molar mixing ratio of 1:1 (acid-to-salt) as a function of reaction time.

Fructose conversion was almost steady for the entire reaction timescale. As illustrated in Figure 4.3, it can be seen very clearly that most of the fructose was converted during the first 10 min of the reaction time, after which the fructose conversion remained almost constant from 10 to 120 min. The yield and selectivity of 5HMF show similar trends to each other. A 5HMF yield of 57.5% was obtained at 10 min reaction time, and then increased to 63.7% at 30 min. The selectivity showed a slight increase from 65.5% at 10 min to 68.3% at 30 min. Over the course of 40 to 120 min reaction time, the yield and selectivity did not show a definite trend, except for wavering around 70% yield ± 10%. This could be attributed to the possible rehydration of 5HMF as a result of producing water as a by-product from the dehydration reaction and the formation of side products by degradation (Zhao et al., 2011). The fluctuation in the 5HMF yield and selectivity when the reaction time was prolonged over 40 min could be related to the decomposition of 5HMF. The decomposition of the 5HMF in acidic medium can occur in three different ways (Asghari and Yoshida, 2007): the first possibility is the rehydration of 5HMF to levulinic and formic acids as a result of the accumulation of the water produced as a by-product from the reaction; the second possibility is decomposition of the 5HMF in a form of condensation reaction by the self-polymerisation between its molecules to produce soluble humins; and the third possibility is the disappearance of 5HMF caused by the cross-polymerisation between the molecules of 5HMF and fructose, thus producing insoluble humins (Kuster, 1990, Chheda and Dumesic, 2007, Asghari and Yoshida, 2007). Also, (Asghari and Yoshida, 2007) reported that the changing of the sample colour to darker brown is a sign of the formation of humins and polymers. In this work, it was observed that the sample colour changed to a darker brown with increasing reaction time, which makes the second and the third possibilities the most likely causes of the fluctuation in 5HMF yield. Consequently, the large molecular weight component and the

intermolecular interactions within the DES contributed to its high viscosity relative to conventional solvent such as water (Mjalli and Naser, 2015). Due to this high viscosity, an internal resistance to shear stress is experienced by the mixture. Typical viscosity for ChCl based DESs ranges from 22 to 821 cP depending on the mole ratio of the composing constituents, composition and temperature (Mjalli and Naser, 2015). However, an increase in temperature weakens the intermolecular forces and, hence, the viscosity decreases. But in this study, the experiments were carried at relatively mild temperatures such as 80 ºC, as consequence the effect of viscosity could be experienced though not investigated. Therefore, the wavering in 5HMF yield and selectivity could be attributed to the highly viscous nature of the ChCl based DES used that may have affected the mass transfer during the reaction, which is expected since the study was carried out in an open batch system. Hence, a dip can be observed at 60 min for the conversion of fructose, which corresponds to the peaks for 5HMF yields and selectivity (Figure 4.3). For this reason, a reaction time of 60 min was selected as the optimum reaction time.

Comparing these results with the literature, this system was very efficient with 87.8% of fructose converted in the first 10 min of the reaction time at 80 °C. Zhao et al. (2011) achieved a fructose conversion of 78% to 5HMF after 60 min of reaction time in a biphasic system and catalysed by a solid heteropolyacid catalyst ($Cs_{2.5}H_{0.5}PW$) at 115 °C. Another study conducted by (Wang et al., 2011) found that fructose conversion to 5HMF in DMSO and a Lewis acid of scandium triflate reached 89.6% at 40 min and 100% at 70 min. Qi et al. (2009a) mentioned that the change in sample colour was a sign of humins formation, which could be attributed to the cross-polymerisation between 5HMF and fructose molecules. Furthermore, it was reported that the 5HMF selectivity in a sucrose dehydration reaction in an ionic liquid decreased after 30 min of reaction time, which was attributed to the decomposition of 5HMF (Chinnappan et al., 2015).

4.3.3 The Effect of Reaction Temperature

The effect of reaction temperature on the fructose conversion, 5HMF yield and selectivity in dehydration reactions of fructose to 5HMF was investigated over a temperature range of 50 to 110 °C, with a feed ratio of 5, reaction time of 60 min, a DES molar mixing ratio of 1:1 (p-TSA to ChCl) and agitation speed of 300 rpm, with the results presented in Figure 4.4. It is worth mentioning that the experiment started when the temperature inside the reaction beaker was the same as that of the oil bath temperature in which it was placed.

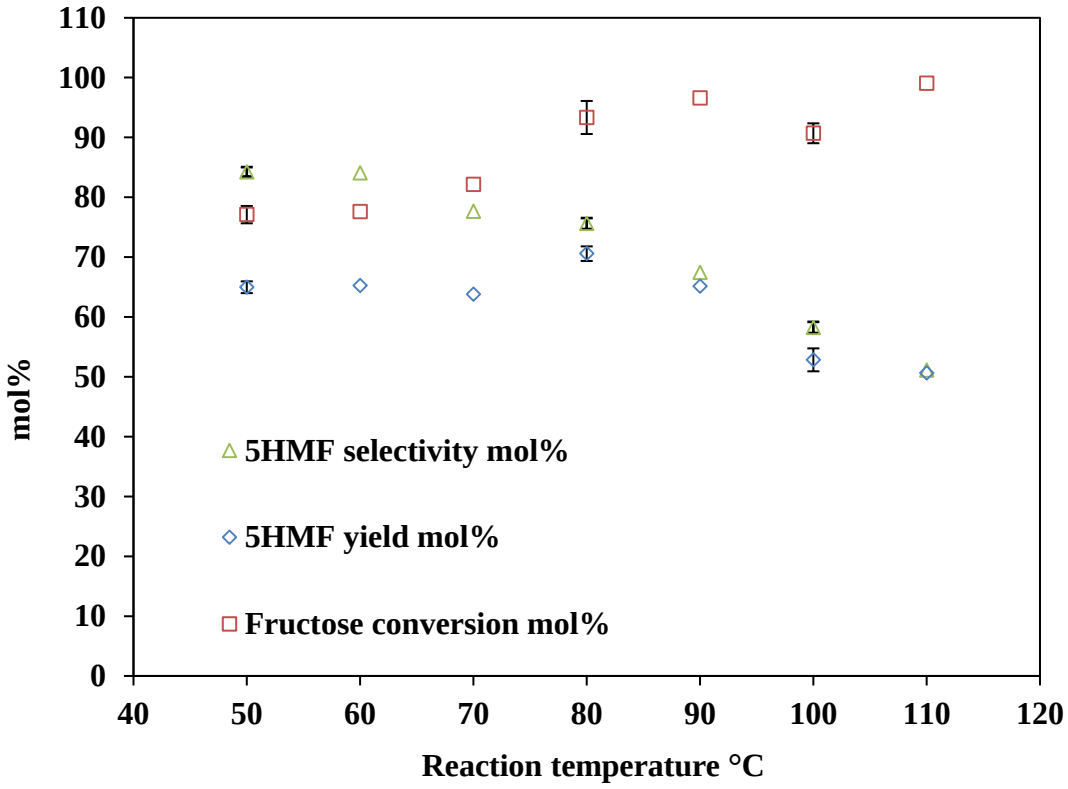


Figure 4.4. The effect of reaction temperature on fructose conversion, 5HMF yield and selectivity at reaction time 60 min, with a feed ratio of 5, agitation speed 300 rpm, and DES mixing ratio of 1:1 (acid-to-salt) at atmospheric pressure.

It can be observed in Figure 4.4 that fructose conversion increased with increasing reaction temperature. Notably, the fructose conversion increased with temperature from 77.1% at 50 °C to 99% at 110 °C. This represents an additional 22% fructose conversion over a 60 °C temperature increase. This increased conversion is because of higher temperatures promoting faster molecular collisions, and therefore increased reaction rates (see Chapter Seven for further details). On the other hand, the 5HMF yield increased gradually as the temperature increased from 50 to 80 °C, thereafter it decreased with a further increase in temperature from 80 to 110 °C. Notably, the highest yield of 70.6% was obtained at 80 °C. The lowest yield of 50.6% was achieved at 110 °C, where the sample colour was very dark brown. This observed change in colour to very dark brown as the reaction temperature increased from 50 to 110 °C is similar to that observed when increasing the feed ratio and increasing the reaction time reported in sections 4.3.1 and 4.3.2, respectively. This could be due to the thermal degradation of 5HMF to humins with increasing reaction temperature (Mittal et al., 2012). Based on these results, 80 °C was selected as the optimum reaction temperature, because it gave the optimal yield of the desired product 5HMF.

The 5HMF selectivity is also presented in Figure 4.4, which shows a general decrease with increasing reaction temperature. The highest 5HMF selectivity was 84.3% at 50 °C, while the lowest selectivity of 51.1% was observed at 110 °C. This could be attributed to the decomposition of 5HMF due to side reactions in the form of polymerisation and rehydration occurring at increasing reaction temperatures (Yang et al., 2015). As the main interest of this chapter is to determine the best reaction conditions which lead to the highest yield of 5HMF, based on the results presented in sections 4.3.1,

4.3.2 and 4.3.3 thus far, a feed ratio of 5, reaction time of 60 min and reaction temperature of 80 °C gave the optimal yield of 5HMF.

Comparing these results with the literature, (Qi et al., 2008) conducted fructose dehydration to 5HMF in an aqueous system catalysed by ion exchange resin using a microwave. They found that the fructose conversion increased from 14.5 to 59.1% when the reaction temperature increased from 100 to 120 °C. A further increase in the temperature to 180 °C led to an increase of the fructose conversion to 94.2%. The same authors later reported a dehydration of fructose to 5HMF in [BMIM]Cl catalysed by Amberlyst resin. It was found that the fructose conversion increased from 52.9 to 90.7 and 98.7% with the increase in reaction temperature from 70 to 80 and 90 °C, respectively (Qi et al., 2009a). In the same publication, they found that the 5HMF selectivity decreased from 93 to 87.4 and 84.6% when the reaction temperature was increased from 70 to 80 and 90 °C, respectively.

Yang et al. (2015) reported that increasing the reaction temperature from 120 to 180 °C led to fructose conversion of 98.8 and 99.9%, and to a 5HMF yield which decreased from 63 to 60 and 54% as the temperature increased from 140 to 160 and 180 °C, respectively, in 15 min of reaction time when fructose was dehydrated to 5HMF in a biphasic system composed of water/THF and catalysed by $FePO_4$. The reduction in 5HMF yield was attributed to the degradation of 5HMF with increasing reaction temperature.

Wang et al. (2011) described a fructose dehydration to 5HMF catalysed by $Sc(OTf)_3$ in DMSO for 120 min. They found that increasing the reaction temperature from 90 to 120 °C increased the 5HMF yield from 66.4 to 83.3%, respectively. However, further increase in temperature decreased the 5HMF yield to 77.8% and changed the sample colour to darker brown. They suggested this decrease in 5HMF yield resulted from the self-polymerisation of 5HMF or by the cross-polymerisation between fructose and

5HMF. This suggestion was based on the fact that the polymers and humins are dark brown in colour, and the reaction mixture colour became darker with increased reaction temperature.

In another work conducted by (Li et al., 2013), fructose was dehydrated to 5HMF in an ionic liquid with an ion exchange resin as a catalyst. It was found that the 5HMF yield increased in the beginning with increasing reaction temperature and subsequently decreased when the reaction time was extended. They attributed the decrease in 5HMF yield to the possible rehydration of 5HMF caused by the water generated from the dehydration reaction as a by-product. In contrast, (Qu et al., 2012) reported different results showing that the 5HMF yield increased with increasing reaction temperature when fructose was dehydrated to 5HMF in sec butanol and $[MIMPS]_3PW_{12}O_{40}$ as a catalyst for 120 min. This could be attributed to the role of the butanol as an in-situ extraction solvent and the efficiency of the solid catalyst. The same conclusion was reported in a different study by (Liu et al., 2012) where, during the dehydration of fructose in a DES composed of ChCl and carbon dioxide, it was found that the 5HMF increased from 30 to 72% when the reaction temperature was increased from 20 to 120 °C. This means the nature of the reaction system plays an essential role; in this case, the 5HMF yield increased in the reported temperature range because it had not yet reached the degradation point.

Zhao et al. (2011) stated that the changing of the sample colour could indicate the occurrence of side reactions such as polymerisation. They found that the 5HMF selectivity decreased with increasing reaction temperature when they conducted 30% fructose solution dehydration reactions at temperatures from 100 to 145 °C in MIBK and catalysed by heteropolyacid. This decrease is attributed to the activation of the side reactions caused by increasing the reaction temperature and the production of insoluble humins as by-products. Fan et al. (2011) reported fructose dehydration to 5HMF in a biphasic system

composed of water/MIBK at a reaction time of 60 min. They found that the 5HMF selectivity increased from 76.8 to 94.6% when the reaction temperature was increased from 100 to 115 °C, and then decreased to 87.9% when the reaction temperature increased to 130 °C, when insoluble by-products were produced. Gomes et al. (2015) carried out a dehydration of a fructose solution with a concentration of 125 g/L in a biphasic system composed of water/acetone (1:1 v/v) and catalysed by H_3PO_4. They found that the 5HMF selectivity increased from 9.7 to 57% as the reaction temperature increased from 120 to 200 °C, respectively. Again, this trend is related to the nature of the reaction medium, where the aqueous system normally requires a high reaction temperature.

4.3.4 The Effect of DES Molar Mixing Ratio

The DES molar mixing ratio was calculated as the p-TSA moles divided by the moles of ChCl, as shown in Equation (A-5) (Appendix A). The effect of the DES molar mixing ratio on the fructose conversion, 5HMF yield and selectivity was investigated at a reaction temperature of 80 °C, reaction time of 60 min, with a feed ratio of 5 and agitation speed of 300 rpm. The results are presented in Figure 4.5.

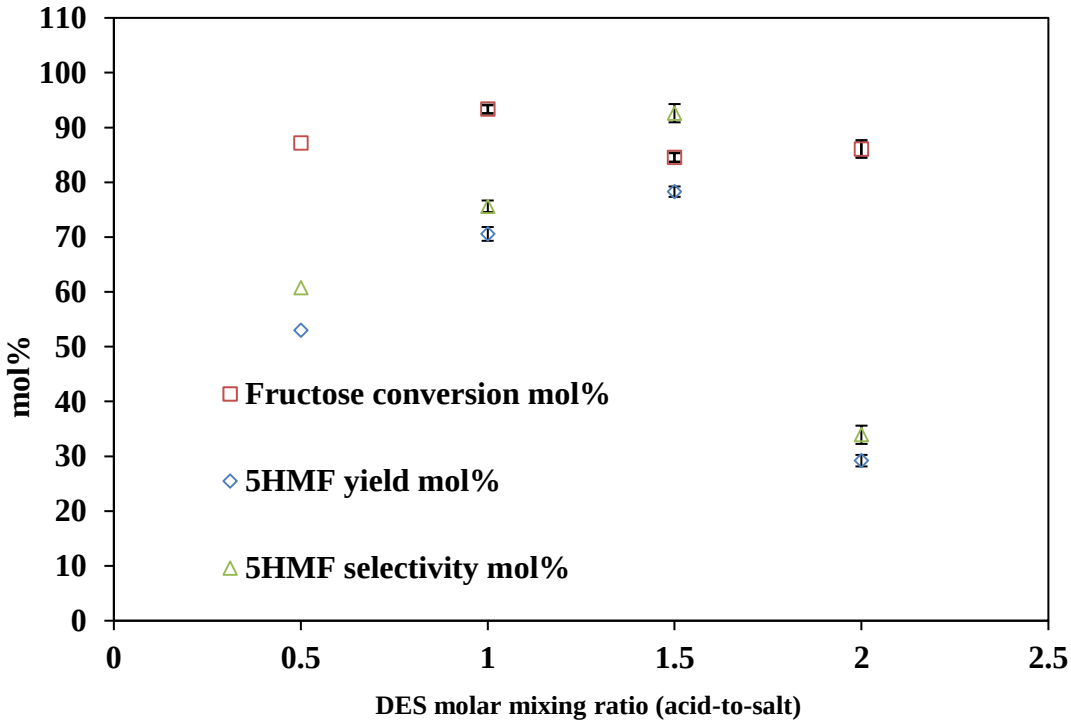


Figure 4.5. The effect of DES molar mixing ratio (acid-to-salt) on fructose conversion, 5HMF yield and selectivity at reaction time of 60 min, reaction temperature of 80 °C, with a feed ratio of 5, and agitation speed 300 rpm at atmospheric pressure.

The conversion of fructose increased as the DES molar mixing ratio increased from 0.5:1 to 1:1, and thereafter decreased when the DES molar mixing ratio was further

increased from 1:1 to 2:1, (This is consistent with the results reported by Tao et al. (2011) which mentioned in section 2.3 (Chapter Two)). It can be observed that the DES molar mixing ratio had a great effect on the 5HMF yield and selectivity in the fructose dehydration reactions, since DES plays a dual role as solvent and catalyst. It was found that as the ratio (acid-to-salt molar ratio) increased from 0.5:1 to approximately 1.5:1, the yield of 5HMF (78.3%) and selectivity (92.6%) increased to the optimum values and thereafter decreased as the ratio was further increased from 1.5:1 to 2:1. The yield increased from 53% at a molar mixing ratio (acid-to-salt) of 0.5:1 to 70% at 1:1 molar mixing ratio, reaching a value of 78.3% at the molar mixing ratio of 1.5:1. On the other hand, when the molar mixing ratio of the DES increased to 2:1, a severe decrease in the 5HMF yield down to 29.2% was observed. A similar effect of the DES ratio on yield was seen on the 5HMF selectivity. The lowest selectivity of 33.9% was obtained at the 2:1 molar mixing ratio, while the highest selectivity of 92.6% was obtained at the 1.5:1 molar mixing ratio. The highest yield of 5HMF was achieved at the molar mixing ratio of 1.5:1; therefore, this is the optimum ratio for the dehydration reactions at these conditions.

According to the findings reported by (Zhang et al., 2012b), which are listed in Table 2.13 (entries 4, 5 and 6), these findings show that increasing the ratio of the HBD in the DES mixture increases the viscosity of the reaction mixture, which may lead to poor mass transfer within the reaction medium. This could result in decreasing the 5HMF yield and selectivity. The other possibility could be the DES used was playing a dual role as a catalyst and solvent, and the changing of the ratio was achieved by increasing the acid ratio, thus decreasing the pH of the reaction medium. Therefore, the severe decrease in 5HMF yield at a DES molar mixing ratio of 2:1 could be attributed to the increase of the acidity of the reaction mixture, leading to the activation of side reactions as a result of the abundance of catalyst sites resulting from the increased acid ratio. A similar assumption

was reported by De Souza et al. (2012), who dehydrated fructose to 5HMF at 150 °C and 120 min reaction time in formic acid as a catalyst in an aqueous medium. They found that the 5HMF yield increased from 3 to 50 and 55% when the formic acid concentration increased from 0 to 10 and 20 wt%, respectively, after which the 5HMF yield decreased severely to 28 and 8% when the formic acid concentration was further increased to 50 and 100 wt%, respectively. They referred this sharp decrease in 5HMF yield to the strong acidity of the reaction medium, which led to the esterification of 5HMF. A similar conclusion was reported by Takeuchi et al. (2008), who stated that the higher acidity leads to the rehydration of 5HMF to formic acid and levulinic acid. This suggestion was previously mentioned by (Kuster and van der Steen, 1977), who reported that a reaction mixture with pH value below 2.7 will favour the rehydration reactions. Furthermore (De Souza et al., 2012) investigated the effect of changing the concentration of lactic acid from 0 to 20 and 50 wt%, and found that the 5HMF yield increased from 4 to 50 and 64%, respectively. This means that the type and the nature of the catalyst is a core point for the dehydration reaction of fructose to 5HMF.

Qi et al. (2008) reported that increasing the solid catalyst resin of Amberlyst15 dosage to 0.02, 0.04, 0.08 and 0.1 g led to an increase in fructose conversion to 25, 90, 98 and 100%, respectively, when the fructose was dehydrated to 5HMF at 80 °C and over a reaction time of 5 min.; they also observed that there was no fructose conversion when the reaction was run for 20 min without a catalyst. Furthermore, this study reported that increasing the resin dosage from 0.02 to 0.04 g led to an increase in the 5HMF yield from 25.5 to 81.6%. However, when the resin dosage was further increased to 0.1 g there was only a slight change in the 5HMF yield to 82%. This may be attributed to the activity of the catalyst sites. Qi et al. (2008) also stated that the catalyst dosage was calculated as a ratio of the fructose mass to the resin mass ($g.g^{-1}$), and found that increasing the resin

dosage from 0.5:1 to 2:1 decreased the 5HMF selectivity from 89.6 to 79.3%. However, a different observation was noticed for the fructose conversion in this chapter, namely that a further increase in the DES ratio over 1.5:1 and 2:1 led to a slight decrease in fructose conversion, which could be attributed to the cross-polymerisation between 5HMF and substrate fructose due to the increasing acid dose in the DES mixture (acid-to-salt ratio) used (Note that the salt amount was fixed while the acid amount was adjusted). The observed colour changes to dark brown confirmed this notion.

Yang et al. (2015) studied the effect of increasing the amount of Fe PO_4 as a catalyst on the dehydration of fructose to 5HMF in a biphasic system of water and THF in the presence of NaCl at 140 °C and 15 min of reaction time. They observed that the fructose conversion increased from 58 to 99% when the Fe PO_4 amount increased from 0.02 to 0.25 g. However, a similar conversion of 93.6% was achieved at a lower temperature of 80 °C in the current study.

Thombal and Jadhav (2014) investigated the effect of the concentrations of a variety of chloride and mineral acid catalysts on the dehydration of fructose to 5HMF in nitromethane as a solvent at a reaction time of 180 min and a reaction temperature of 100 °C. They found that increasing the concentration of the catalysts decreased the 5HMF yield and increased the yields of some by-products (although the by-products themselves were not specified by the authors). The concentration of 10 wt% gave the optimum yield of 5HMF. Gomes et al. (2015) investigated the effect of increasing the concentration of H_3PO_4 on 5HMF selectivity in the fructose dehydration to 5HMF reaction in a biphasic system of water and acetone at a reaction temperature of 180 °C. They reported that increasing the acid concentration from 0.5 to 1.5% increased the 5HMF selectivity from 43 to 57%. A further increase in acid concentration led to a decrease in 5HMF selectivity due to the rehydration of 5HMF, which is consistent with the results reported in this section.

4.4 Conclusions

The DES mixture of ChCl and p-TSA was found to be a highly promising catalytic solvent mixture for the reactions of fructose dehydration to 5HMF, giving high yields and selectivity. The dehydration process using such a mixture was found to be efficient as the DES mixture comprised renewable, non-toxic and cheap materials. The process did not require severe reaction conditions as the reactions were conducted at 80 °C, 60 min and atmospheric pressure. The highest yield obtained was 78.3% with selectivity of 92.64% and fructose conversion of 84.5% at a feed ratio of 5, a DES molar mixing ratio of 1.5:1, 80 °C, agitation speed of 300 rpm and 60 min of reaction time.

Chapter 5 Effect of Salt-Modified DES on Fructose Dehydration to 5HMF

5.1 Abstract

In Chapter Four, the effects of reaction temperature, time, feed ratio (fructose-to-DES ratio) and DES molar mixing ratio were reported. In this chapter, the results from the investigation of the effect of using N,N-diethylenethanol ammonium chloride (DEAC) ($C_6H_{16}ClNO$) in place of the choline chloride (ChCl) used in Chapter Four while the acid component remains p-toluenesulfonic acid monohydrate (p-TSA) ($C_7H_8O_3S$) are presented. The results of the salt-modified DES were compared with the previous DES system discussed in Chapter Four. It was found that a fructose conversion of 88.6% with a 5HMF yield of 84.8% was achieved at a reaction temperature of 80 °C, reaction time of 60 min, a DES molar mixing ratio of 1:1 (p-TSA-to-DEAC), agitation speed of 300 rpm and initial fructose ratio of 5 at atmospheric pressure. Although a change in the process behaviour was observed upon changing the DES composition, a similar operating condition to that presented in Chapter Four was achieved. The optimum DES molar mixing ratio (acid-to-salt ratio) was found to be 0.5:1, rather than the 1.5:1 obtained in Chapter Four

5.2 Introduction

One of the major challenges associated with the dehydration of carbohydrates to furans is the elimination of side reactions, which cause low yields of furans (Agirrezabal-Telleria et al., 2014). For this reason, researchers have sought an efficient and inexpensive reaction media to produce 5HMF from biomass (Knochel, 1999). The use of DES as a reaction media in the organic synthesis has proven to be effective for green synthesis and low-cost production (Handy, 2015). The concept of the eutectic mixture involves

generating a homogeneous mixture in a liquid form by heating and stirring their respective solid forms (Smith et al., 2014). This liquid mixture has a reduced melting point at a specific eutectic temperature and mixing ratio (see Chapter one, Section 1.4.5 for details). . However, organic solvents have a negative environmental impact and the use of water also promotes side reactions, whereas mixing the two components (ChCl and p-TSA) together at a ratio of 1:1 generates a homogeneous DES, which has a freezing point of 2.7 °C (Zhao et al., 2015). Thus, the use of DESs as a reaction media has brought several advantages over the use of water or organic solvents, such as the ability to dissolve fructose and avoid the rehydration of 5HMF, and also the fact that the reaction can be conducted at mild reaction conditions. Furthermore, the performance of the DES as a reaction medium is governed by its composition and mixing ratios. These factors highly influence the properties of the DES such as the melting point, density, and viscosity (as listed in Table 2.12 and Table 2.13). Therefore, the effect of the DES composition on fructose dehydration reactions was investigated in this chapter.

5.3 Results and Discussion

The results obtained by substituting the ChCl with (DEAC) ($C_6H_{16}ClNO$) and p-toluene sulfonic acid monohydrate (p-TSA) ($C_7H_8O_3S$) to produce a salt-modified DES are presented in the following sections. In turn, the effects of the feed ratio, reaction time, reaction temperature and DES molar mixing ratios are discussed. While other process variables were held constant, the variable of study was adjusted, from which the point that gave the highest yield of 5HMF was chosen as the optimum operating condition.

5.3.1 The Effect of Feed Ratio

The effect of the feed ratio (fructose-to-DES) was studied in a ratio range of 2.5 to 100, a reaction time of 60 min, a reaction temperature of 80 °C, a DES mixing molar ratio

of 1:1 (acid to salt), an agitation speed of 300 rpm and under atmospheric pressure. The results are shown in Figure 5.1. The conversion of fructose increased from 92 to 97.6%, as the feed ratio increased from 2.5 to 5, respectively. Thereafter, the fructose conversion remained at approximately 98% for the rest of the feed ratios used. It is therefore clear that the feed ratio (fructose-to-DES) has little or no effect on the conversion of fructose.

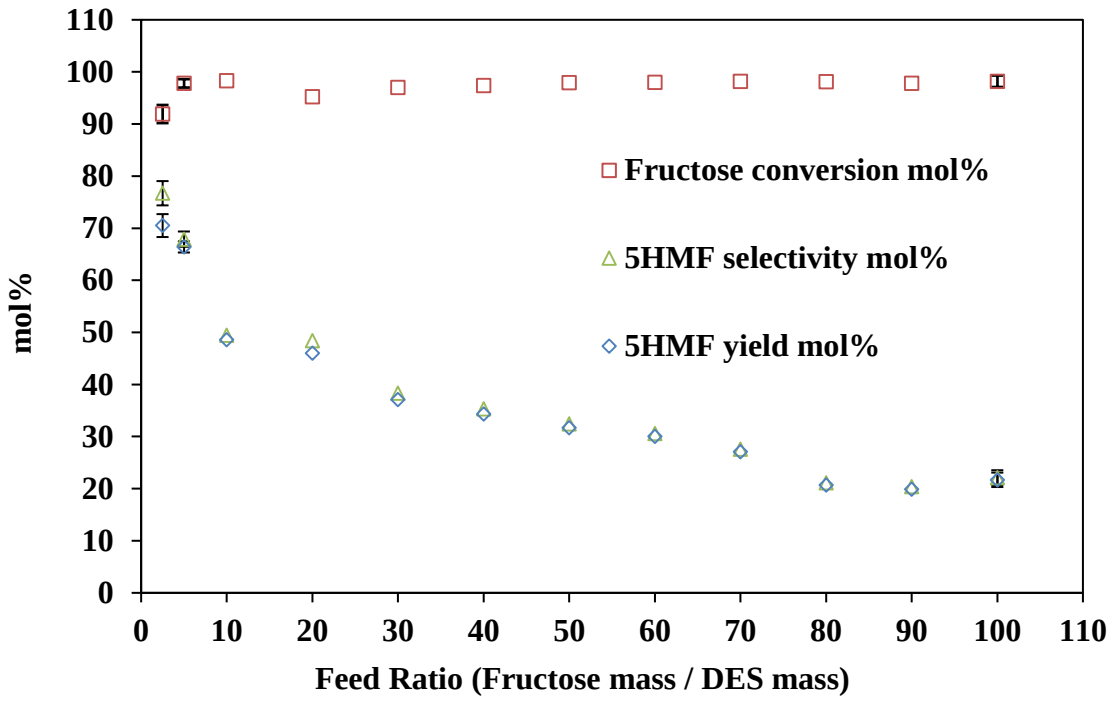


Figure 5.1. The effect of the feed ratio on fructose conversion, 5HMF yield and selectivity at 60 min, 80 °C, DES mixing molar ratio of 1:1 (acid-to-salt), agitation speed of 300 rpm and at atmospheric pressure.

Unlike the fructose conversion, the feed ratio (fructose-to-DES) greatly influenced the 5HMF yield and selectivity. The yield and selectivity follow an approximately identical trend. The 5HMF yield and selectivity rapidly decreased with increasing feed ratio in the range of 2.5 to 10, and thereafter gradually decreased with further increases in

the feed ratio. This could be attributed to the polymerisation reactions (Van Putten et al., 2013) and/or the rehydration of the 5HMF produced caused by the presence of water generated from the fructose dehydration reaction. This can be controlled by incorporating an efficient separation technique to remove the 5HMF produced or the water from the reaction medium. The highest yield of 5HMF obtained was 70.5% at a feed ratio of 2.5, with a selectivity of 76.7%. However, when the feed ratio increased from 5 to 20, the 5HMF yield decreased from 66.4 to 45% while the selectivity decreased from 67.9 to 48.4%, respectively.

The lowest 5HMF yield obtained was 21.7%, with a selectivity of 22.1% at a feed ratio of 100. The standard deviation in 5HMF yield obtained upon using a feed ratio (fructose-to-DES) of 2.5 was highest compared to that obtained at the feed ratio of 5 for triplicate experiments. However, the feed ratio of 5 was chosen as the reproducibility was better compared to the one at feed ratio of 2.5. Similarly, the sample colour changed to darker brown upon increasing the initial feed ratio, which could indicate the occurrence of side reactions (possibly single or cross-polymerisation) producing humins and polymers (Hu et al., 2015). Despite the substituted ChCl with DEAC in the salt-modified DES, a similar observation to that reported in Chapter Four was noticed. Humins are dark brown solid compounds that appear as a by-product in sugar dehydration reactions. These side reactions could have caused the reduction in 5HMF yield and selectivity observed (Figure 5.1). The effect of the feed ratio on fructose conversion, 5HMF yield and selectivity is similar to the trend observed in the previous DES system in Chapter Four, showing that changing the organic salt has no significant effect on the dehydration reaction with increased feed ratio.

These results are comparable with those reported by (Hu et al., 2015) when they studied the effect of the initial fructose concentration (feed ratio) on the dehydration

reaction of fructose to 5MHF, catalysed by a magnetic lignin-derived catalyst in a DMSO as a solvent at a reaction temperature of 130 °C and a reaction time of 40 min. It was found that increasing the initial concentration of fructose had a negative effect on the 5HMF yield. As the initial concentration of fructose was increased from 2 to 15 wt%, the 5HMF yield gradually decreased from 83.7 to 75.6%, respectively. On the other hand, the conversion of fructose reached 100% and remained the same as the initial concentration increased from 2 to 10 wt%. Further increases in the initial concentration of fructose to 12 and 15 wt% led to a slight decrease in fructose conversion to 98.4 and 96.7%, respectively. The reduction in yield and conversion was linked to the activation of side reactions in the form of the self-polymerisation of fructose and cross-polymerisation between 5HMF and fructose to produce humins. Using the salt-modified DES in this research has achieved a similar conversion, 5HMF yield and selectivity but at a lower temperature of 80 °C, while maintaining the environmental and economic advantages.

5.3.2 The Effect of Reaction Time

Figure 5.2 shows respectively the influence of reaction time on the 5HMF yield, selectivity, and fructose conversion over the time range from 5 to 120 min at 80 °C, with a feed ratio of 5, agitation speed of 300 rpm and a DES molar mixing ratio of 1:1 (p-TSA-to-DEAC) at atmospheric pressure. Except the 5HMF yield, instability can be observed in the fructose conversion and 5HMF selectivity as the reaction time increases. Notably, the fructose conversion and 5HMF selectivity trend are approximately a mirror image, such that a high conversion of fructose led to low 5HMF selectivity. Unlike in Chapter Four, where the fructose conversion was reasonably stable while 5HMF selectivity was fluctuate as the reaction time increased. Therefore, since the experimental conditions were the same with the difference being the substituted ChCl with DEAC in the salt-modified DES, it

follows that the instability in the fructose conversion and 5HMF selectivity noticed in Figure 5.2 can be attributed to the properties of the salt-modified DES (see Chapter 8 for further details).

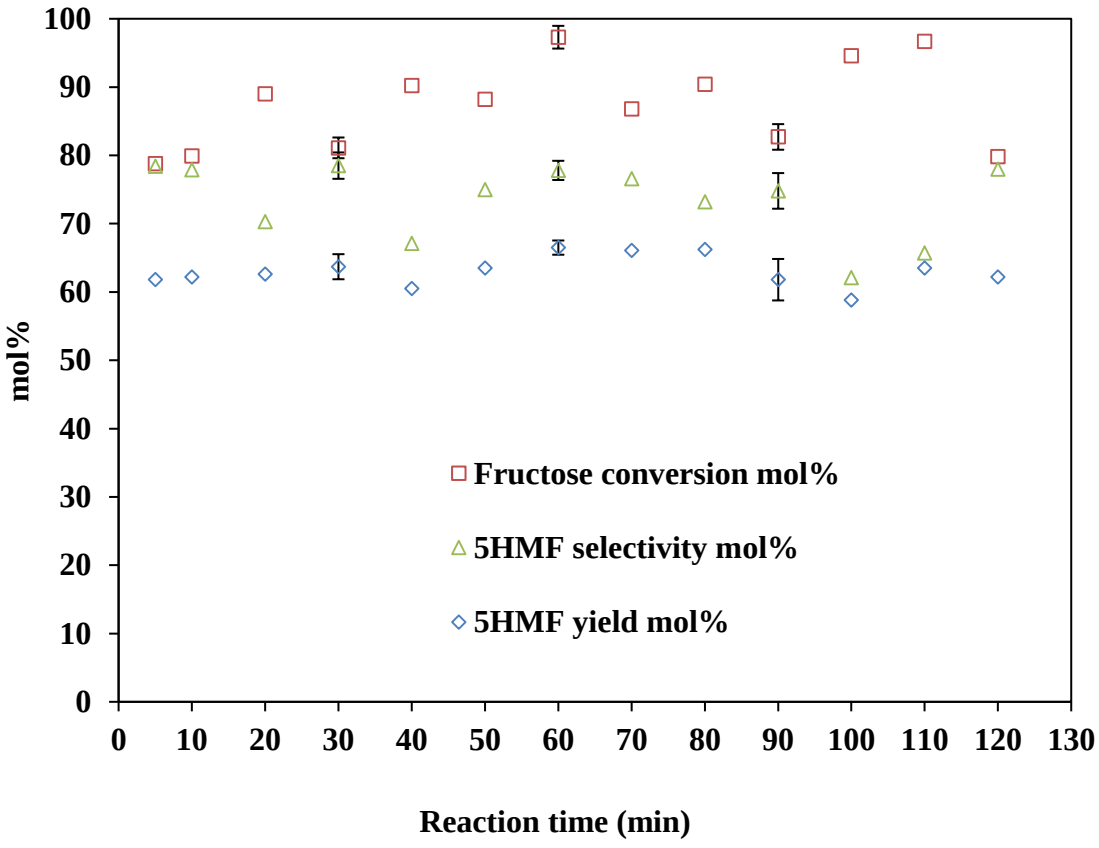


Figure 5.2. The effect of reaction time on fructose conversion, 5HMF yield and selectivity at 80 °C, with a feed ratio of 5, agitation speed of 300 rpm and DES molar mixing ratio of 1:1 (p-TSA-to-DEAC) at atmospheric pressure.

The results illustrated in Figure 5.2 revealed that the 5HMF yield varied from 58.8 to 66.5%, while the 5HMF selectivity was slightly changing in a narrow range from 62.1 to 78.4% with increased reaction time. The reaction time slightly affected the fructose conversion, as it was varied from 78.8 to 97.3%. This may be attributed to the poor mass

transfer profile resulting from changing the organic salt of the DES used. This could have affected the properties of the DES and slowed the kinetics of the dehydration reactions, possibly leading to the activation of side reactions such as the rehydration of 5HMF. As the prolonging of the reaction time could lead to the occurrence of more by-products, a reaction time of 60 min was chosen as the optimum reaction time. Comparing this system with the previous DES system in Chapter Four, the fructose conversion, 5HMF yield and selectivity trends in this system (salt-modified DES) were wavering differently. This may be related to the different DES composition.

Generally, the nature of the reaction medium governs the behaviour of the dehydration reaction. Hafizi et al. (2016) investigated the effect of reaction time on fructose dehydration to 5HMF, using DMSO as a solvent and a prepared solid catalyst of mesoporous silica and sulphonic acid at 165 °C. The results obtained showed that over 95% of the fructose was converted in the first 30 min of the reaction time. As the reaction time reached 60 min, the fructose was completely converted. On the other hand, the reaction time showed a different influence on 5HMF yield and selectivity. As the reaction time increased to 30 min, a maximum yield and selectivity of 74.2 and 77.8% were achieved, respectively. However, in this chapter, the highest 5HMF yield obtained was 66.5% at a reaction temperature of 80 °C and 60 min relative to 74.2% achieved at 165 °C and 30 min by Hafizi et al. (2016). This shows that with the salt-modified DES, a high 5HMF yield can be achieved at milder reaction conditions than the severe conditions reported in the literature. Furthermore, extending the reaction time to 300 min showed a gradual decrease in both 5HMF yield and selectivity (Hafizi et al., 2016), while the formation of some by-products such as humins and soluble polymers was observed, confirming that extending the reaction time generally leads to the occurrence of side reactions like condensation and polymerisation.

5.3.3 The Effect of Reaction Temperature

The effect of reaction temperature on the fructose dehydration reactions using a salt-modified DES mixture of DEAC and p-TSA was investigated, with the results of the fructose conversion, 5HMF selectivity and yield presented in Figure 5.3. The following reaction conditions were used: a DES mixing molar ratio of 1:1 (acid-to-salt), reaction time of 60 min, with a feed ratio of 5, reaction temperature range of 50 to 110 °C and agitation speed of 300 rpm at atmospheric pressure.

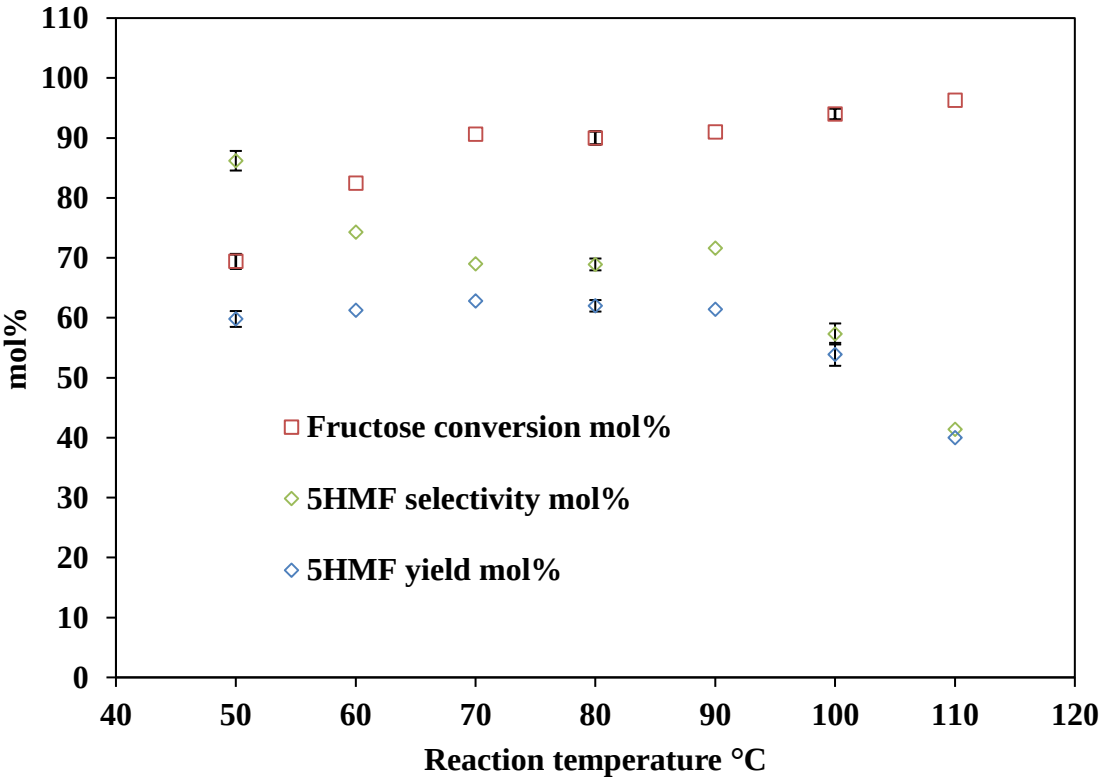


Figure 5.3. The effect of reaction temperature on fructose conversion, 5HMF yield and selectivity at 60 min, with a feed ratio of 5, agitation speed of 300 rpm and DES molar mixing ratio of 1:1 (p-TSA-to-DEAC) at atmospheric pressure.

While the fructose conversion increased with increasing reaction temperature, the 5HMF yield remained almost constant at approximately 61% when the reaction temperature was increased from 50 to 90 °C, and decreased thereafter as the temperature was increased from 90 to 110°C. It varied from 59.8% to 62.8%, while the 5HMF selectivity decreased from 86.2% at 50 °C to 68.9% at 80 °C. A further decrease in 5HMF yield and selectivity was shown when the reaction temperature was increased to 100 and 110 °C: the yield of 5HMF decreased to 53.9% at 100 °C with a selectivity of 57.3%, while the lowest yield of 5HMF obtained was 40% at 110 °C, with a selectivity of 41.4%. The change in the sample colour to a darker brown with increasing reaction temperature could be attributed to the thermal degradation of 5HMF to humins upon increasing the reaction temperature (Gomes et al., 2017). This is consistent with the observation reported in Chapter Four. Fructose conversion increased from 69.4% at 50 °C to 96.3% at 110 °C. A reaction temperature of 80 °C was chosen as the optimum reaction temperature, since this temperature gave a high yield of 5HMF of 62%. Comparing the effect of the reaction temperature on the fructose conversion, 5HMF yield and selectivity with the previous DES in Chapter Four, the trends were generally similar.

Gomes et al. (2017) studied the effect of the reaction temperature on the dehydration reaction of fructose to 5HMF. The study was conducted in a DMSO as a solvent and phosphotungstic acid as a catalyst in a temperature range from 100 to 140 °C. The results revealed that when the reaction was performed with only the DMSO (without the catalyst), the conversion of fructose was completed at 40 °C, and therefore further increasing the reaction temperature to 140 °C had no influence on fructose conversion. On the other hand, 5HMF yield started to increase from 0 (10 °C) to 80% (80 °C), after which it remained constant (80%) as the reaction temperature further increased to 140 °C. These results are attributed to the high solubility of fructose in DMSO, and the ability of the latter

to act as a catalyst and to stabilise the positively charged fructose intermediates while hindering their side reactions. When the reaction was catalysed by 10% of phosphotungstic acid, the conversion of fructose was complete as the reaction temperature reached 10 °C, while the 5HMF increased to 92% as the reaction temperature reached 30 °C, and remained steady as the temperature increased to 100 °C. Further increase in the temperature to 140 °C decreased the 5HMF yield to 80%, due to the activation of side reactions (5HMF degradation). Despite the high yield of 5HMF obtained, the use of DMSO and phosphotungstic are faced with an environmental footprint and cost, while the use of the salt-modified DES resolved these challenges, except that a lower 5HMF yield (62% at 80 °C) was achieved. This suggested the need to modify the DES composition and experimental conditions to maximise the yield of 5HMF.

5.3.4 The Effect of DES Molar Mixing Ratio

The DES mixing ratio is a key variable in the production of 5HMF by this reaction medium. As the acid p-TSA is the active side in the DES, the acid ratio was changed every time, while the salt molar ratio was fixed at 1. In this chapter, different molar mixing ratios were investigated. They are 0.5:1, 1:1, 1.5:1 and 2:1 (p-TSA-to-DEAC). The DES molar mixing ratio had a significant effect on 5HMF yield and selectivity. The effect of the salt-modified DES mixing ratio is presented in Figure 5.4. Fructose conversion increased from 88.6 to 97.8% as the salt-modified DES mixing ratio increased from 0.5:1 to 1:1 (acid-to-salt ratio) and decreased from 97.8 to 91.5% as the mixing ratio increased further from 1:1 to 1.5:1; it remained at 91.6% for the DES mixing ratios of 1.5:1 and 2:1.

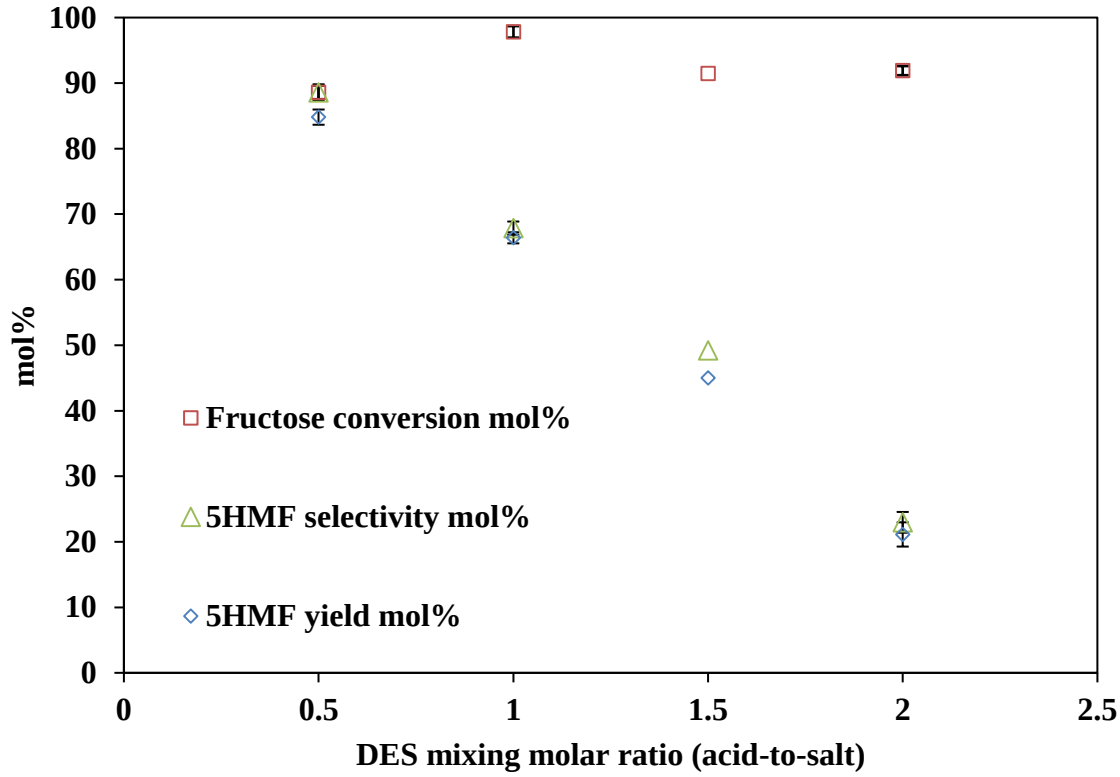


Figure 5.4. The effect of DES molar mixing ratio on fructose conversion, 5HMF yield and selectivity at 60 min, with a feed ratio of 5, and agitation speed of 300 rpm at atmospheric pressure.

Both the 5HMF yield and selectivity sharply decreased upon increasing the p-TSA acid molar ratio (Figure 5.4). At a molar mixing ratio of 0.5:1 (acid-to-salt), the highest 5HMF yield of 84.8% was obtained with a 5HMF selectivity of 88.6%. As the mixing ratio increased to 1:1, the 5HMF yield decreased down to 66.4%, with a 5HMF selectivity of 67.9%. When the mixing ratio was further increased to 1.5:1, a lower 5HMF yield of 45% was obtained with a 5HMF selectivity of 49.2%. The lowest 5HMF yield obtained was 21.1%, along with the lowest 5HMF selectivity of 23% at a mixing ratio of 2:1.

The effect of the salt-modified DES molar mixing ratio on 5HMF yield and selectivity in this system was entirely different to the effect of the DES molar mixing ratio in the previous system in Chapter Four. The difference in the trends can be attributed to the DES composition, which resulted in changes in the DES properties because of the different ionic interaction between the ions and cations of the DES components. Therefore, the dehydration reaction behaved differently, thus showing that the composition of the DES plays a key role in the fructose dehydration reactions to 5HMF in DES. The effect of the different DES compositions described in Chapters Four, Five and Six is presented and discussed in Chapter Eight of this study.

Zhang et al. (2017) reported a similar trend for the effect of catalyst loading on the conversion of glucose to 5HMF, catalysed by prepared solid catalyst consists of silica, aluminium and phosphoric acid and a mixture of water and γ-valerolactone (GVL) as a solvent at a reaction temperature of 170 °C. It was found that increasing the catalyst loading from 10 to 30 mg increased the 5HMF yield from 65 to 93% and selectivity from 72 to 90%, respectively. The increase was attributed to the increased in the number of active sites of the catalyst used. Further increase in catalyst loading over 30 mg led to a decrease in the 5HMF yield and selectivity, due to the increased activity of the catalyst, which could have activated the degradation reactions (the by-products were not specified). The conversion of glucose was increased from 88 to 100% by increasing the catalyst loading from 10 to 30 mg. Further increases in catalyst loading did not influence the conversion of glucose. This difference in observations on the conversion of the biomass to the one reported in this section (Figure 5.5) could be attributed to the difference in the feedstock (glucose and fructose), experimental conditions and also the reaction medium.

5.4 Conclusions

The DES was modified by replacing the ChCl with DEAC, and the effect of this change in the DES composition was investigated. How the salt-modified DES influences the operating conditions previously achieved in Chapter Four was evaluated. Also, how the salt-modified DES affects the best reaction conditions reported in Chapter Four was investigated. The highest yield of 5HMF obtained was 84.8% with a selectivity of 88.6% at the optimum reaction conditions: reaction temperature of 80 °C, reaction time of 60 min, DES mixing ratio of 0.5:1 (p-TSA-to-DEAC), agitation speed of 300 rpm and a feed ratio of 5. It was found that with the salt-modified DES the mixing ratio was lower at 0.5:1, compared to the 1.5:1 obtained in Chapter Four. The salt-modified DES at a mixing ratio of 0.5:1 (acid-to-salt) gave 84.8% 5HMF yield compared to the 78.3% obtained with the 1.5:1 from the DES used in Chapter Four. The effect of the DES molar mixing ratio on the 5HMF yield and selectivity behaved completely differently compared to the previous DES system in Chapter Four, which could be attributed to the different organic salt used, resulting in a change in the behaviour of the ionic interaction between the HBD and the hydrogen acceptor. This affected the dehydration reaction of fructose to 5HMF.

Chapter 6 Effect of Acid-Modified DES on Fructose Dehydration to 5HMF

6.1 Abstract

In Chapter Five, the salt component of the DES was replaced to produce a salt-modified DES. However, in this chapter the acid component (p-TSA) of the DES used in Chapter Four is replaced with adipic acid, while the ChCl is still retained to form an acid-modified DES, which is used for the dehydration of fructose to 5HMF. The adipic acid component of the acid-modified DES acts as an HBD and the ChCl as an organic salt. The influence of this change in the DES composition on the optimum reaction conditions of the process relative to those obtained in Chapters Four and Five is investigated in this chapter. The acid-modified DES gave a fructose conversion of 100%, while the 5HMF yield and selectivity were approximately 91% at the mild reaction conditions of 90 °C reaction temperature and atmospheric pressure, a DES molar mixing ratio of 1:1 (acid-to-salt), agitation speed of 300 rpm, initial fructose ratio of 2.5 and reaction time of 120 min. It was found that with the acid-modified DES 100% conversion of fructose was achieved, resulting from a shift in the best condition to 90 °C and 120 min relative to the 80 °C and 60 min observed in Chapters Four and Five, respectively. Despite the high yield of 5HMF observed, the shift of optimum condition towards a higher temperature and reaction time would incur additional operating costs.

6.2 Introduction

The use of different acidic catalysts' systems prepared from renewable sources in the 5HMF synthesis through fructose dehydration was reported by (Hu et al., 2008). They tested a variety of carboxylic acids such as malonic acid, citric acid and oxalic acid, from which they found the most efficient catalyst. Those carboxylic acids were studied as an

active site of catalyst, when combined with choline chloride to form DES. The optimum results obtained were 91.8% conversion of fructose and 83.8% selectivity of 5HMF, when a DES of ChCl and citric acid was used in an ethyl acetate/renewable IL biphasic system at 80 °C and 60 min (Hu et al., 2008).

In this chapter, the results obtained after the acid component of the DES used in Chapter Four was replaced by adipic acid are presented and discussed. The acid-modified DES (ChCl as organic salt and adipic acid as a weak dicarboxylic acid) acts as an HBD as well as a catalyst for the dehydration reaction of fructose to 5HMF. This novel acid-modified DES is considered cheap, green and renewable; the adipic acid can be produced from biomass sources, as shown in Figure 6.1. The relatively high melting point of the acid-modified DES used in this chapter (85 °C at a mixing ratio of 1:1), compared to a DES composed of citric acid and ChCl, which has a melting point of 69 °C at the same mixing ratio (Zhang et al., 2012b), could affect its viscosity. The 5HMF yield obtained by using the acid-modified DES was similar to the one obtained from citric acid and ChCl reported by Hu et al. (2008), even without the use of any extraction solvents. The best reaction conditions leading to a high 5HMF yield and selectivity of 90.8% with 100% fructose conversion were found to be at a reaction time of 120 min, a feed ratio of 2.5, agitation speed of 300 rpm and a reaction temperature of 90 °C.

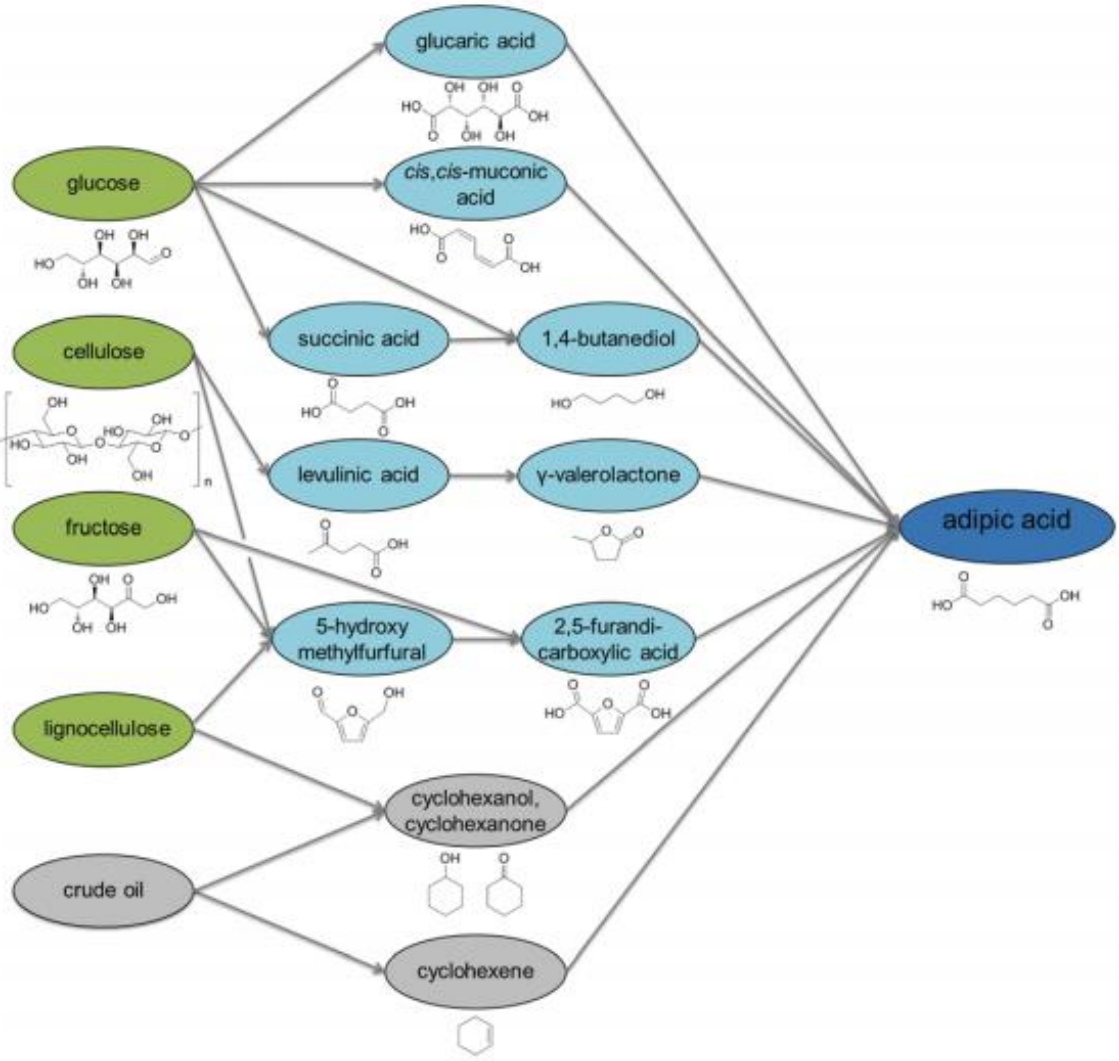


Figure 6.1. The production of adipic acid from different resources (Beerthuis et al., 2015)

6.3 Results and Discussion

As in Chapters Four and Five, the effects of the different reaction parameters (the feed ratio, reaction time, reaction temperature and DES molar mixing ratios) on the dehydration reaction of fructose to 5HMF were examined in order to establish the role of the acid component of the DES and its influence on the reaction conditions, especially the

optimum reaction conditions. The results are presented in a similar manner to Chapters Four and Five.

6.3.1 The Effect of Reaction Time

The reaction time establishes the extent of time the reaction molecules have contact or collide to form a product. This shows that it is a key factor that influences the rate of the reaction. Figure 6.2 shows the effect of the reaction time on the fructose conversion, 5HMF yields and selectivity in the dehydration of fructose using acid-modified DES over a time range of 30 to 180 min, at a reaction temperature of 90 °C, a feed ratio of 5, agitation speed of 300 rpm and a DES molar mixing ratio of 1:1 (adipic acid-to-ChCl), at atmospheric pressure.

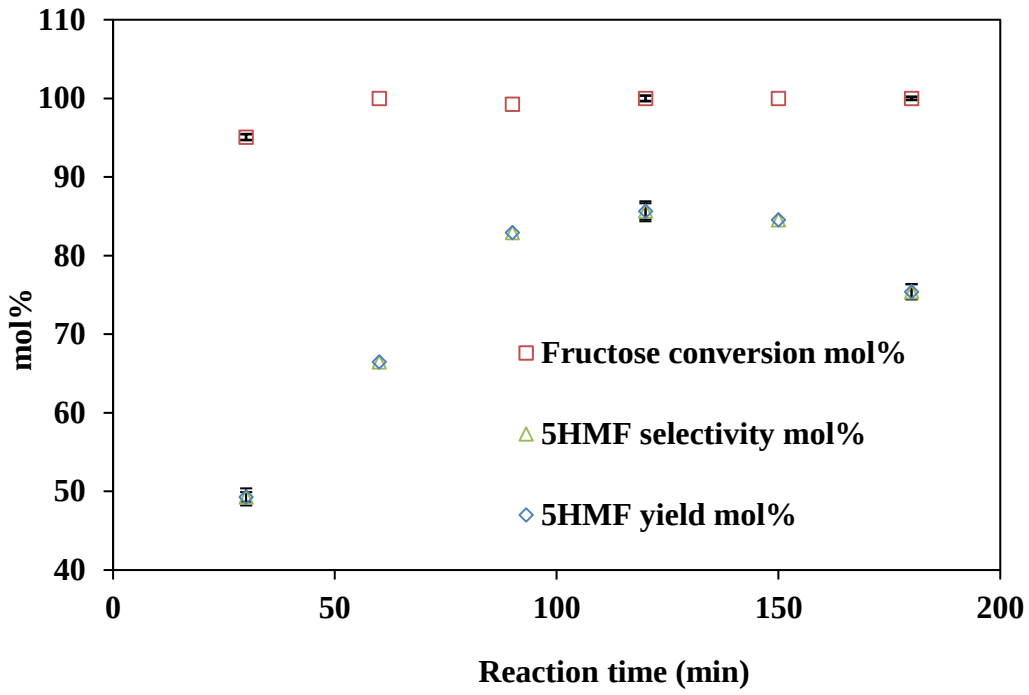


Figure 6.2. The effect of reaction time on fructose conversion, 5HMF yield and selectivity at a temperature of 90 °C, with a feed ratio of 5, agitation speed of 300 rpm and DES molar mixing ratio of 1:1 (adipic acid-to-ChCl), at atmospheric pressure.

As the reaction time increased from 30 to 60 min, the fructose conversion increased gradually from 95 to 100%, and remained at 100% with further increase in the reaction time from 60 to 180 min. Note that the longer time range used in this chapter was chosen based on the pre-investigation experimental plan. The 5HMF yield and selectivity showed approximately identical trends to each other. The 5HMF yield and selectivity increased readily from 49.3% to approximately 83%, as the reaction time increased from 30 to 90 min, thereafter plateauing at approximately 85.6% over the reaction time range of 90 to 150 min, and then gradually decreasing over the reaction time range of 150 to 180 min to a

value of 75.4%. It can be observed that the 5HMF yield was lowest at the shortest reaction time of 30 min.

The observed trends in both the 5HMF yield and selectivity while the fructose conversion remained at approximately 100% could be as a result of the occurrence of side reactions due to 5HMF decomposition to several by-products such as levulinic acid, formic acid and humins (Pawar and Lali, 2014). Hence, 120 min was obtained from Figure 6.2 as the best reaction time for fructose dehydration reaction to 5HMF using acid-modified DES. This represents twice the best reaction time obtained in Chapters Four and Five, which could be due to the high melting point of the final DES. The DES melting points were 2.7 °C (DES, Chapter Four), 38 – 45 °C (salt-modified DES, Chapter Five) and 85 °C (acid-modified DES, Chapter Six), while the respective reaction temperatures were 80, 80 and 90 °C. The closeness between the reaction temperature for the acid-modified DES and its melting point could have increased the optimum reaction time. Additionally, adipic acid is a weak dicarboxylic acid compared to the strong p-TSA Brønsted acid used in the DES in Chapters Four and Five; hence, its partly dissociate in the reaction media and release some of its hydrogen atoms. Thus, it showed lower capability and activity than a stronger acid in terms of proton donor, this caused it requiring a longer reaction time to achieve a higher yield.

Comparing these results with the two previous DES systems in Chapter Four and Chapter Five, the fructose conversion in this system was more stable and complete. The 5HMF yield and selectivity showed a sharp increase as the reaction time increased from 30 to 90 min. The different trend observed in this system could be attributed to the different composition of the DES used and the high thermal activity of the dehydration reaction under a higher reaction temperature and a longer reaction time. While similar behaviours have been reported in the literature, the dehydration reaction reported in this chapter was

carried out at milder reaction conditions, in an environmentally friendly reaction medium and produced a higher 5HMF yield without using extraction solvents.

Kilic and Yilmaz (2015) investigated the effect of reaction time on the fructose conversion and 5HMF selectivity in the fructose dehydration to 5HMF in a reaction time range from 0 to 180 min, using three different systems of catalysts in DMSO as a solvent at a reaction temperature of 110 °C. Firstly, they studied the effect of reaction time on the fructose conversion in different homogeneous catalysts: HCl, H_2SO_4 and H_3PO_4. They found that the conversion of fructose reached 90% in a reaction time of less than 1 min and reached 100% after 30 min. The conversion continued at 100% along the time range to 180 min. Secondly, the effect of reaction time on the fructose conversion was investigated over a variety of heterogeneous sulfonated catalysts such as SO_4/TiSBA-15, $SO_4/TiO_2{-}SiO_2$, SO_4/SiO_2, SO_4/AC and SO_4/ZrO_2. They found that the SO_4/ZrO_2 was the most active catalyst and the conversion of fructose was completed in 50 min, whereas the other catalysts were found to have lower activity and the conversion was slower, only gradually increasing with reaction time. Thirdly, the conversion of fructose was only tested in a DMSO as a solvent without using any catalyst. It was found that the conversion of fructose gradually increased from 0 to 50% as the reaction time increased from 0 to 180 min. When H_3PO_4 was used as a catalyst, the 5HMF selectivity increased from 21 to 80% as the reaction time increased from 1 to 120 min, after which the 5HMF selectivity decreased to 55% due to the rehydration of 5HMF, and produced levulinic acid and formic acid as by-products when the reaction time was further increased to 180 min. When H_2SO_4 was used as a catalyst the 5HMF selectivity increased from 20 to 83%, as the reaction time increased from 1 to 150 min, respectively, after which the selectivity decreased to 75% when the reaction time further increased to 180 min. The selectivity gradually increased from 21 to 75% as the reaction time increased from 1 to 180 min,

when HCl was used as a catalyst. The acid-modified DES can therefore achieve similar conversion, 5HMF yield and selectivity (Figure 6.2) to the aqueous systems reported above, but with the benefit of mild experimental conditions and environmental friendliness.

Liu et al. (2015) studied the effect of reaction time on 5HMF yield in the fructose dehydration reaction to 5HMF in a DMSO and prepared ionic liquid $[4.2H][HSO_4]_2$ as a reaction medium over a reaction time range from 30 to 120 min and reaction temperature of 90 °C. It was found that the 5HMF yield increased from 92 to 94% as the reaction time increased from 30 to 60 min, respectively. A further increase in reaction time to 120 min decreased the 5HMF yield to 89%. The decrease in 5HMF yield was attributed to the formation of humins and the rehydration of 5HMF to levulinic acid and formic acid as a result of extending the reaction time, particularly at higher reaction temperatures. It is clear, therefore, that the result obtained using an acid-modified DES is in line with results reported in the literature; DES, however, has the benefit of both solvent and catalyst at mild reaction conditions.

6.3.2 The Effect of Feed Ratio

The effect of the feed ratio (fructose-to-acid-modified DES) on the fructose dehydration reaction to 5HMF was studied using a feed ratio ranging from 2.5 to 20 at the optimum reaction time of 120 min (Figure 6.2), a reaction temperature of 90 °C, a DES molar mixing ratio of 1:1 (acid-to-salt), agitation of 300 rpm and at atmospheric pressure. Figure 6.3 shows the results obtained. Unlike the fructose conversion reported in Chapter Four for the use of DES, which increased as the feed ratio increased from 2.5 to 20, it is clear that with the acid-modified DES, fructose conversion remained at approximately 100% for all the feed ratios (fructose-to-acid-modified DES).

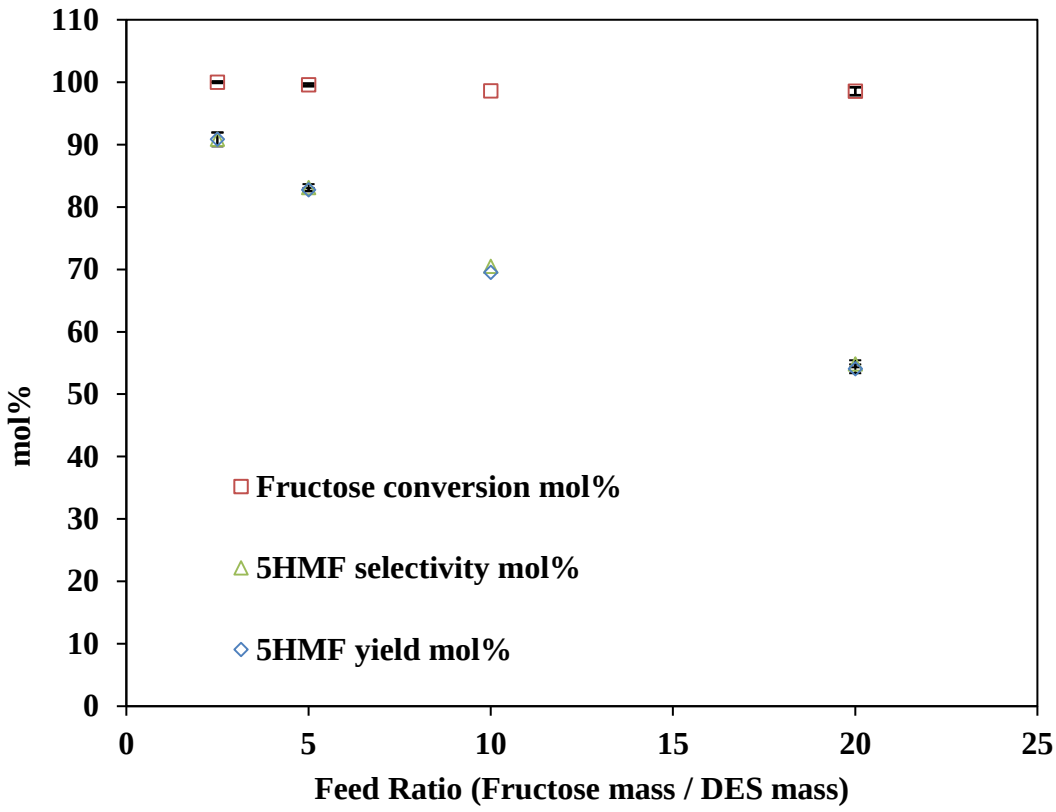


Figure 6.3. The effect of feed ratio on fructose conversion, 5HMF yield and selectivity at reaction time of 120 min, reaction temperature of 90 °C, DES molar mixing ratio of 1:1 (acid-to-salt), and agitation of 300 rpm at atmospheric pressure.

From Figure 6.3, the high conversion of fructose observed in all the feed ratios used can be attributed to the higher reaction temperature used in this acid-modified DES system. On the other hand, the 5HMF yield and selectivity was highly influenced by the feed ratio, as shown in Figure 6.3. It can be seen that the 5HMF yield and its selectivity readily decreased as the feed ratio increased from 2.5 to 20. The trends in both 5HMF yield and selectivity were almost identical. The 5HMF yield decreased from 90.8% at 2.5 feed ratio to 82.8% at a feed ratio of 5. A further decrease in 5HMF yield was noticed

from 69.5 to 54.1%, when the feed ratio was increased from 10 to 20 (fructose-to-acid-modified DES). A similar trend was observed in 5HMF selectivity, which decreased from 90.8 to 54.9% when the feed ratio was increased from 2.5 to 20.

The results of fructose conversion, 5HMF yield and selectivity obtained with the acid-modified DES (ChCl and adipic acid) in this system are similar to those observed with the DES (ChCl and p-TSA acid) used in Chapter Four. It is worth mentioning here that this system was more stable (less fluctuating) in terms of 5HMF yield, selectivity, and fructose conversion at a feed ratio of 2.5 compared to the previous DES systems. This could be due to the different DES composition, which led to changes in the DES properties in which the use of adipic acid in the acid-modified DES could have contributed to the stability of the dehydration reaction. It has been reported in the literature that the decrease in 5HMF yield and selectivity could be related to the activation of side reactions (fructose polymerisation) as a result of increasing the feed ratios (Xu et al., 2015a). The results in Figure 6.3 are in line with this observation, where the highest 5HMF yield and selectivity occurs at the low feed ratio of 2.5.

A similar trend was reported by (Xu et al., 2015a), who observed that the 5HMF yield decreased from 72 to 30% and the 5HMF selectivity decreased slightly from an initial level of 77%, as the fructose concentration increased from 0.05 to 0.2 g/ml upon the dehydration of fructose to 5HMF in a DMSO as a solvent and (M-ZrPO-0.75) as a solid catalyst at a reaction time of 30 min and a reaction temperature of 80 °C. Also reported was a change in the colour of the reaction medium to a darker brown as the initial concentration of fructose was increased. They attributed this to the occurrence of side reactions that produced soluble polymers and humins. However, the decrease in fructose conversion was attributed to the deactivation of the heterogeneous catalyst used. The use of acid-modified DES eliminated the challenges of catalyst deactivation observed with the

heterogeneous catalyst and a higher 5HMF yield of 91% was achieved at a reaction temperature of 90 °C and time of 120 min. These results are in agreement with that reported by (Ma et al., 2015). However, they conducted their experiment for 30 min and at a reaction temperature of 110 °C, using isopropanol as a solvent and ionic liquid ([HO_2CMMIm]Cl) as a catalyst. The decrease in 5HMF yield was also attributed to polymerisation and rehydration side reactions, leading to the production of humins as a by-product.

6.3.3 The Effect of Reaction Temperature

The effect of reaction temperature on the fructose dehydration reaction was studied for the acid-modified DES in the range of 80 to 120 °C. It is worth mentioning here that the choice of 80 °C as the start temperature for the acid-modified DES was based on the observations from the dehydration reactions carried out from 60 to 70 °C, which yielded little or no 5HMF. Therefore, a higher range of reaction temperatures was needed compared to those used in the systems reported in Chapters Four and Five, in order to produce significant 5HMF yield. This can be attributed to the high viscosity and melting point (85 °C) of the acid-modified DES. The remaining experimental factors were set at the optimum conditions obtained from the analysis reported in sections 6.3.1 and 6.3.2. The results are presented in Figure 6.4.

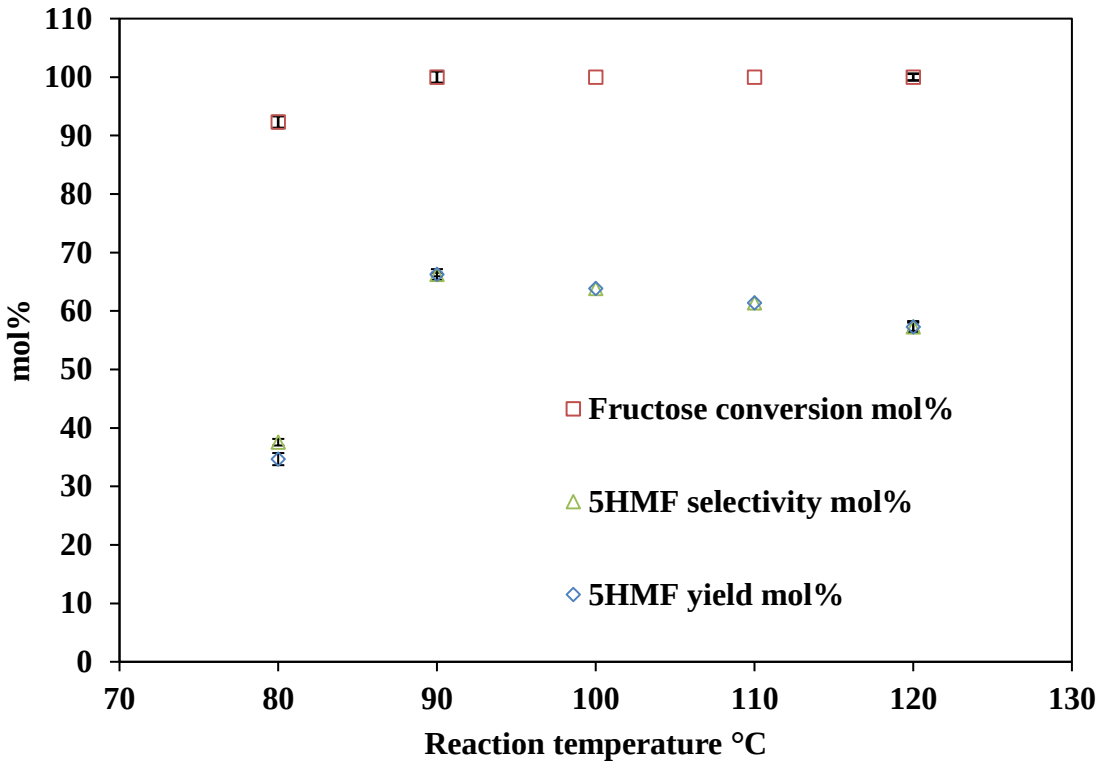


Figure 6.4. The effect of reaction temperature on fructose conversion, 5HMF yield and selectivity at reaction time of 120 min, DES molar mixing ratio of 0.5:1 (acid-to-salt), with a feed ratio of 2.5 and agitation of 300 rpm at atmospheric pressure.

The rise in reaction temperature highly influenced the behaviour of the dehydration reaction of fructose to 5HMF. As the temperature increased from 80 to 90 °C the fructose conversion increased from 92 to 100%, and remained at 100% throughout further increases in the reaction temperature from 90 to 120 °C. This implies that the dehydration reaction of fructose to 5HMF reached completeness at 90 °C, at 120 min, feed ratio (fructose-to-acid-modified DES) of 2.5 and an acid-modified DES molar mixing ratio of 0.5:1. Despite achieving complete conversion at 90 °C, it was worth increasing the 5HMF yield; hence, higher reaction temperatures were tested, as shown in Figure 6.4. This differs from the

trend reported for the DES used in Chapter Four, which has the same organic salt but with a different acid (p-TSA) mixture. While 100% conversion of fructose was achieved at 90 °C for the acid-modified DES, approximately the same conversion was achieved at 110 °C for the DES used in Chapter Four at the same reaction time of 60 min (see Figure 4.4, Figure 6.2 and Figure 6.4).

The 5HMF yield and selectivity follow identical trends as observed in Figure 6.2 and Figure 6.3. As the reaction temperature was increased from 80 to 90 °C, the 5HMF yield increased rapidly from 34.7 to 66.2%, while its selectivity increased from 37.6 to 66.2%. By contrast, when the reaction temperature was increased from 100 to 120 °C, both 5HMF yield and selectivity decreased gradually and equally from 66.3 to 57.3%. Despite the 100% conversion of fructose recorded from 90 to 120 °C, any further increase in reaction temperature beyond 90 °C did not produce a corresponding increase in the 5HMF yield and selectivity, but rather resulted in their decrease. However, as the reaction temperature increased beyond 90 °C, a colour change to darker brown was observed in the reaction media similar to those reported in Chapters Four and Five. Hence, the decreasing 5HMF yield and its selectivity noticed in Figure 6.4 could be a sign of the occurrence of side reactions in a form of polymerisation (Lv et al., 2017) as the reaction temperature increased above 90 °C. Comparing Figure 6.4 (acid-modified DES) and Figure 4.4 (DES), it is clear that by increasing the reaction temperature, the 5HMF yield and its selectivity exhibited different trends. The best reaction temperature, therefore, for the fructose dehydration to 5HMF using an acid-modified DES was considered to be 90 °C, as this gave the highest yield of 5HMF (66.2%). This optimum reaction temperature for the acid-modified DES is different to that obtained by the DES reported in Chapter Four. These results, therefore, show that the composition of the DES plays a key role in determining the best conditions for the dehydration reaction of fructose to 5HMF.

Lv et al. (2017) studied fructose dehydration to 5HMF in an aqueous system catalysed by silica and heteropolyacid. They observed that increasing the reaction temperature from 140 to 180 °C promoted the conversion of fructose from 6 to 100%. The 5HMF yield showed an increase from 4.7 to 50.2% as the reaction temperature increased from 140 to 170 °C, and decreased to 15.3% upon an increase to 180 °C. The selectivity decreased from 78.3 to 15.3% as the reaction temperature increased from 140 to 180 °C. These results are different from the results displayed in Figure 6.4. This is because of the differences in the experimental conditions and catalyst used by Lv et al. (2017) and that employed in this study. Lv et al. (2017), however, observed the production of humins as the reaction temperature increased, which is an indication of the occurrence of side reactions, resulting in the decrease of 5HMF yield and selectivity. A similar decrease can be seen in Figure 6.4 as the reaction temperature increases.

6.3.4 The Effect of DES Molar Mixing Ratio

Figure 6.5 shows the fructose conversion, 5HMF yield and selectivity as influenced by the molar mixing ratio within the acid-modified DES in the dehydration reaction of fructose to 5HMF. The influence of the molar mixing of ChCl and adipic acid to form the acid-modified DES was examined in the range 0.5:1 to 2:1 (acid-to-salt) at the optimum conditions obtained in sections 6.3.1 to 6.3.3.

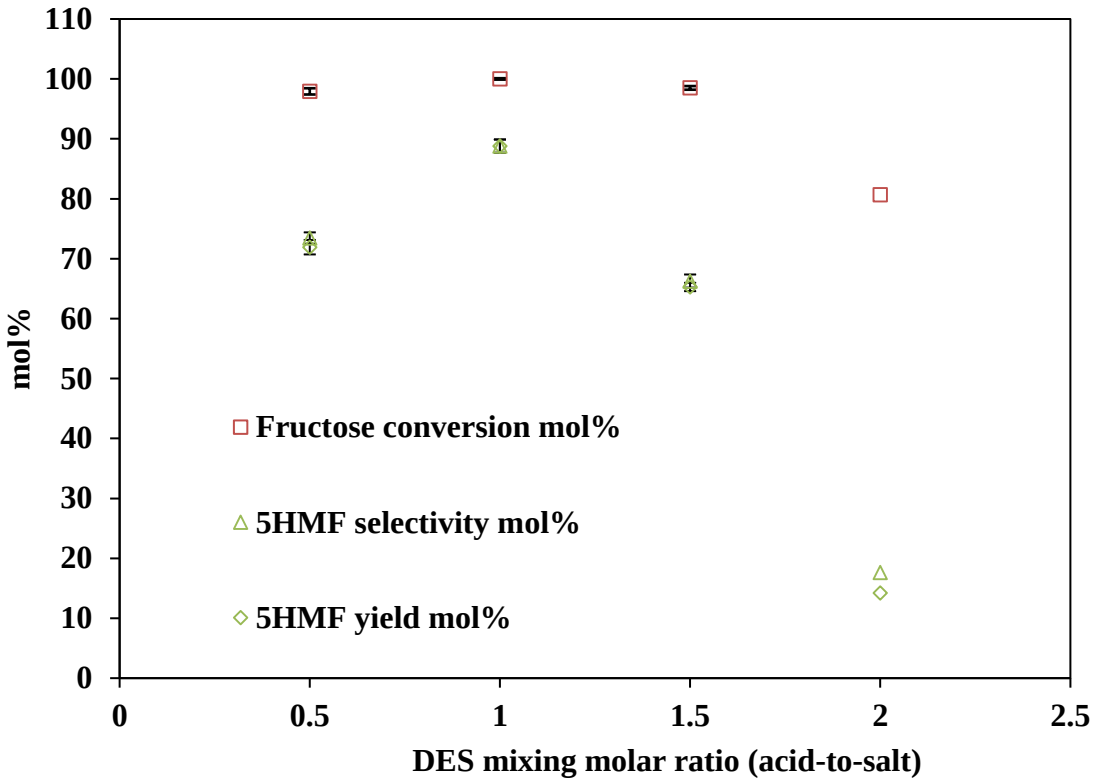


Figure 6.5. The effect of DES mixing ratio (acid moles-to-salt moles) on fructose conversion, 5HMF yield and selectivity at reaction time of 120 min, reaction temperature of 90 °C, with a feed ratio of 2.5 and agitation of 300 rpm at atmospheric pressure.

The conversion of fructose gradually increased from approximately 98% to 100% when the molar mixing ratio (acid-to-salt) within the acid-modified DES was increased from 0.5:1 to 1:1. A further increase to 1.5:1 caused a decrease to 98.5%, and thereafter a sharp decrease in fructose conversion to approximately 81% was observed for a molar mixing ratio of 2:1. This may be attributed to changes in the activity of the acid-modified DES as the adipic acid component increases from 0.5:1 to 2:1, thus increasing the acid sites. When Figure 6.5 is compared with the result for the DES molar mixing ratio

presented in Figure 4.5 (Chapter Four), it shows that a similar trend can be observed in the fructose conversion for the acid-to-salt ratio from 0.5:1 to 1:1, after which the trend differs. This reinforced the effect of the DES composition on the optimum conditions (section 6.3.3). This could be due to the different acid used, which may influence the activity of the DES in terms of the HBD and a catalyst for the dehydration reaction of fructose to 5HMF. The weak dicarboxylic (adipic) acid could affect the interaction between the ions and cations of the acid and the salt, leading to a change in the acid-modified DES properties such as the high viscosity and high melting point.

The influence of the molar mixing ratio of the acid-modified DES on the 5HMF yield and its selectivity is also presented in Figure 6.5. Again, the 5HMF yield and selectivity follow almost identical trends. The 5HMF yield and selectivity both increased rapidly from 72 to 88.8% as the molar mixing ratio was increased from 0.5:1 to 1:1, and thereafter decreased from 88.8 to 14.2% (5HMF yield) and 17.7% (5HMF selectivity) as the acid-modified DES molar mixing ratio was increased from 1:1 to 2:1. The optimum molar mixing ratio of the acid-modified DES was found to be 1:1 (adipic acid-to-ChCl ratio), as this gave a fructose conversion of 100%, a maximum 5HMF yield and selectivity of approximately 89% at 90 °C, 120 min, fructose-to-DES ratio of 2.5 and agitation of 300 rpm at atmospheric pressure. This decrease in 5HMF yield and selectivity at higher molar mixing ratios could be attributed to the composition of the DES and the changes in its properties resulting from changing the molar mixing ratios of the acid to salt. This could lead to side reactions activated by the increasing acid content of the acid-modified DES, which then suppresses 5HMF selectivity. Zhao et al. (2016) observed a comparable trend, when they found that the conversion of fructose increased from 86.5 to 100% as the catalyst loading ratio increased from 5 to 40. Conversely, the 5HMF yield showed an initial increase from 60.7 to 75.4% as the catalyst loading ratio was increased from 5 to 20,

but then decreased to 70.8% with further increase in catalyst loading under conditions of 30 min reaction time, 140 °C temperature, a fructose mass of 500 mg, DMSO as a solvent and sulfonated carbon as a solid catalyst. They attributed the decrease in 5HMF yield with increasing catalyst loading to the abundance in acid sites, which could have induced side reactions such as 5HMF rehydration. The optimum 5HMF yield obtained was 90% at 160 °C and 90 min, compared to 91% achieved with the acid-modified DES at 90 °C and 120 min. Furthermore, Li et al. (2016) reported a similar observation when they conducted a fructose dehydration in GVL and water as a solvent, and with a solid acid catalyst composed of p-TSA and paraformaldehyde (POM). They obtained an optimum yield of 78.1% at 130 °C and 30 min, which is less than that achieved with the acid-modified DES (Figure 4.5 and Figure 6.5). The decrease in 5HMF yield and selectivity noticed in Figure 6.5 as the molar mixing ratio of the acid-modified DES increased is because of the promoted side reactions such as polymerisation, condensation, and rehydration that occur when the catalyst loading is increased (Li et al., 2016).

6.4 Conclusions

An acid-modified DES from Chapter Four was tested for fructose dehydration to 5HMF. The composition of the acid-modified DES was adipic acid and ChCl. The influence of the DES composition was examined over the following ranges: reaction temperature 80 – 120 °C, time 30 –180 min, feed ratio 2.5 – 20 and molar mixing ratio 0.5:1 – 2:1, in order to re-evaluate the best reaction conditions. The best conditions achieved with the acid-modified DES were a temperature of 90 °C, a reaction time of 120 min, a feed ratio of 2.5, agitation speed of 300 rpm and a molar mixing ratio (adipic acid-to-ChCl) of 1:1, at atmospheric pressure. The fructose conversion, 5HMF yield and selectivity achieved at these conditions were 100%, 90% and 90%, respectively. It was

also found that with acid-modified DES the optimum conditions of reaction temperature, time and molar mixing ratio shifted from the 80 °C, 60 min and 1.5:1 obtained for the DES used in Chapter Four. This confirmed that the DES composition greatly influenced the best reaction conditions. Compared to the previous DES system, the acid-modified DES fructose dehydration reaction was more stable in terms of 5HMF yield and selectivity, even at low feed ratios. This system, however, required a higher reaction temperature and longer reaction time to achieve a higher 5HMF yield, selectivity, and fructose conversion. The effect of the DES molar mixing ratio on the 5HMF yield, selectivity and fructose conversion showed different trends compared to previous systems. Increasing the acid moles has a negative effect on the dehydration reaction, possibly changing the behaviour of the ionic interaction between the HBD and the hydrogen acceptor, and thus affecting the dehydration reaction of fructose to 5HMF by activating the side reactions and so decreasing the 5HMF yield, selectivity, and fructose conversion.

Chapter 7 Kinetics of Fructose Dehydration Reactions in DES

7.1 Overview

In this chapter, the chemical kinetics of the fructose dehydration reactions to 5HMF reported in Chapters Four, Five and Six for the different DES solvents are determined. The DES systems in this chapter are designated as follows: DES (DES1), salt-modified DES (DES2) and acid-modified DES (DES3). The effect of the reaction temperature on the reaction rate was fitted with the empirical Arrhenius equation. The activation energy (Ea) and the pre-exponential (or frequency) factor (A) (i.e. a constant that defines the rate due to the frequency of collisions in the system) were determined for each DES system. The reaction rate here is defined as the change in concentration of the fructose with respect to time. Therefore, to determine the reaction rate investigations were carried out in different temperature ranges and at different time intervals. The fructose dehydration reaction has been reported in the literature as a first order reaction for different homogeneous and heterogeneous catalysts (Kuster, 1977, Caratzoulas and Vlachos, 2011, Lee and Wu, 2012). However, in this study it was found that using DES1 and DES2 resulted in first order reactions, while DES3 gave rise to a 1.8 reaction order; the activation energies of their reactions can be summarised as DES1≈DES2<DES3.

7.2 Description of Experimental Work

The chemical kinetics (reaction rates) were determined for the three DESs as follows: for DES1 and DES2, experiments were conducted from 1 to 15 min at 5 min intervals and reaction temperatures of 60, 70 and 80 °C at a molar mixing ratio of 1:1, with a feed ratio of 5, 300 rpm and atmospheric pressure. For DES3, the reaction rate experiments were carried out from 1 to 20 min at 5 min intervals, temperatures 80, 90 and 100 °C, with a feed ratio of 2.5 (fructose-to-DES) and the same conditions of agitation

speed and pressure as DES1 and DES2. The experiments were carried out using an open batch system. The required reaction temperature was maintained for the DES mixture before adding the substrate fructose to the reaction beaker. Time zero was taken immediately after adding the substrate fructose to the DES system. At the end of each reaction time, the reactor was quenched in an ice bath and thereafter the samples were collected and analysed. This cycle was repeated for each experiment. The experimental procedures carried out in this chapter with regard to the preparation of materials and the reaction and analysis routines are the same as those mentioned in Chapter Three. Consequently, the effect of agitation on mass transfer and kinetics was not investigated, since it is a homogeneous system and also the experiments were performed in an open system.

7.3 Fundamental Theory to Determine the Reaction Rate

In this study, a single step reaction of fructose to 5HMF was assumed as unimolecular. It was also assumed that the sum of a series of elementary steps in the reaction system is represented by the overall reaction rate equation. Finally, the steady-state approximation is assumed, which implies that an intermediate in the dehydration reaction is consumed as quickly as it is formed, and its concentration remain the same during the reaction from fructose to 5HMF. The reaction rate of fructose dehydration is assumed as a function of fructose concentration (C) and time (t) as follows:

$$\frac{dc}{dt} = -C_t^{\,n}\, k \qquad (7\text{-}1)$$

Starting from this hypothesis, the reaction rate for the dehydration of fructose to 5HMF was examined by approximating the fructose concentration data with (n) order equation for the three DES systems. The order of reaction with respect to fructose

concentration is estimated based on the best numerical approximation between the experimental fructose concentrations and the ones obtained from Equation (7-2) and Equation (7-3) by using table curve 2D, Jundel software; these equations are the mathematical integration of the differential Equation (7-1).

$$\mathbf{C_t^{(1-n)} = C_0^{(1-n)} - (1-n)kt} \qquad (n\neq 1),\ k\ (mol^{(1-n)}\ L^{(n-1)}\ s^{-1}) \tag{7-2}$$

$$\mathbf{C_t = C_0\, e^{-kt}} \qquad (n=1),\ k\ (s^{-1}) \tag{7-3}$$

where: C_t is the fructose concentration at time (t) in (mM), C_0 the initial fructose concentration in (mM), k the rate constant and (t) the time in (s).

The Arrhenius equation (7-6) was used to estimate the activation energy (Ea) and the frequency (or pre-exponential) factor (A), by plotting the ln k (rate constant) values at different reaction temperatures versus the inverse of the reaction temperature (1/T) for the dehydration reaction of fructose to 5HMF. Where the slope and the intercept of the plots represent the (Ea/R) and ln A in Equation (7-6), respectively. The Arrhenius equation was obtained from (Fogler, 1999), as shown in Equation (7-4).

$$\boldsymbol{k = Ae^{-Ea/RT}} \tag{7-4}$$

where: A is the frequency factor constant for a reaction system (s^{-1}), Ea the activation energy (kJ mol^{-1}), R the gas constant = 8.314 J mol^{-1} K^{-1} and T the absolute temperature in K.

By taking the natural log for both sides of Equation (7-4), Equation (7-5) was obtained

$$\ln k = \ln A - \left(\frac{Ea}{RT}\right) \tag{7-5}$$

By rearranging Equation (7-5), Equation (7-6) was obtained:

$$\ln k = \left(-\frac{Ea}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{7-6}$$

7.4 Kinetics Analysis

The main aim of kinetic analysis is to determine the reaction order of the fructose dehydration reactions and to facilitate in the clarification of reaction mechanisms. This section consists of studies of the fructose dehydration reaction kinetics for the three DES systems used.

7.4.1 Reaction Kinetics of Fructose Dehydration in DES1

The experimental and model data of fructose concentration versus time using DES1 was approximated with Equation (7-3) at the reaction temperatures of 60, 70 and 80 °C to obtain the reaction rate constant (k) and the reaction order (n) at each temperature, as shown in Figure 7.1. The results listed in Table 7.1 and Figure 7.1 revealed that the reactions at the three temperatures can be described by a first order reaction.

Table 7.1. Values of k and n at different temperatures for fructose dehydration reaction using DES1

Temperature °C	Reaction rate constant (k) s^{-1}	Reaction order (n)
60	2.83×10^{-3}	1.0
70	3.83×10^{-3}	1.1
80	5×10^{-3}	1.1

The increasing rate constant (k) with reaction temperature also indicates an increasing rate of reaction. Notably, the temperature dependence of the rate constant can be observed, as the rate constant increases as the reaction temperature increases from 60 to 80 °C at the same initial fructose concentration, pressure, and agitation speed. This explains the increased fructose conversion with increasing reaction temperature observed in Chapter Four for DES1. Also, the results are consistent with the effect of the reaction temperature on the 5HMF yields and selectivity presented in section 4.3.3 at 60, 70 and 80 °C.

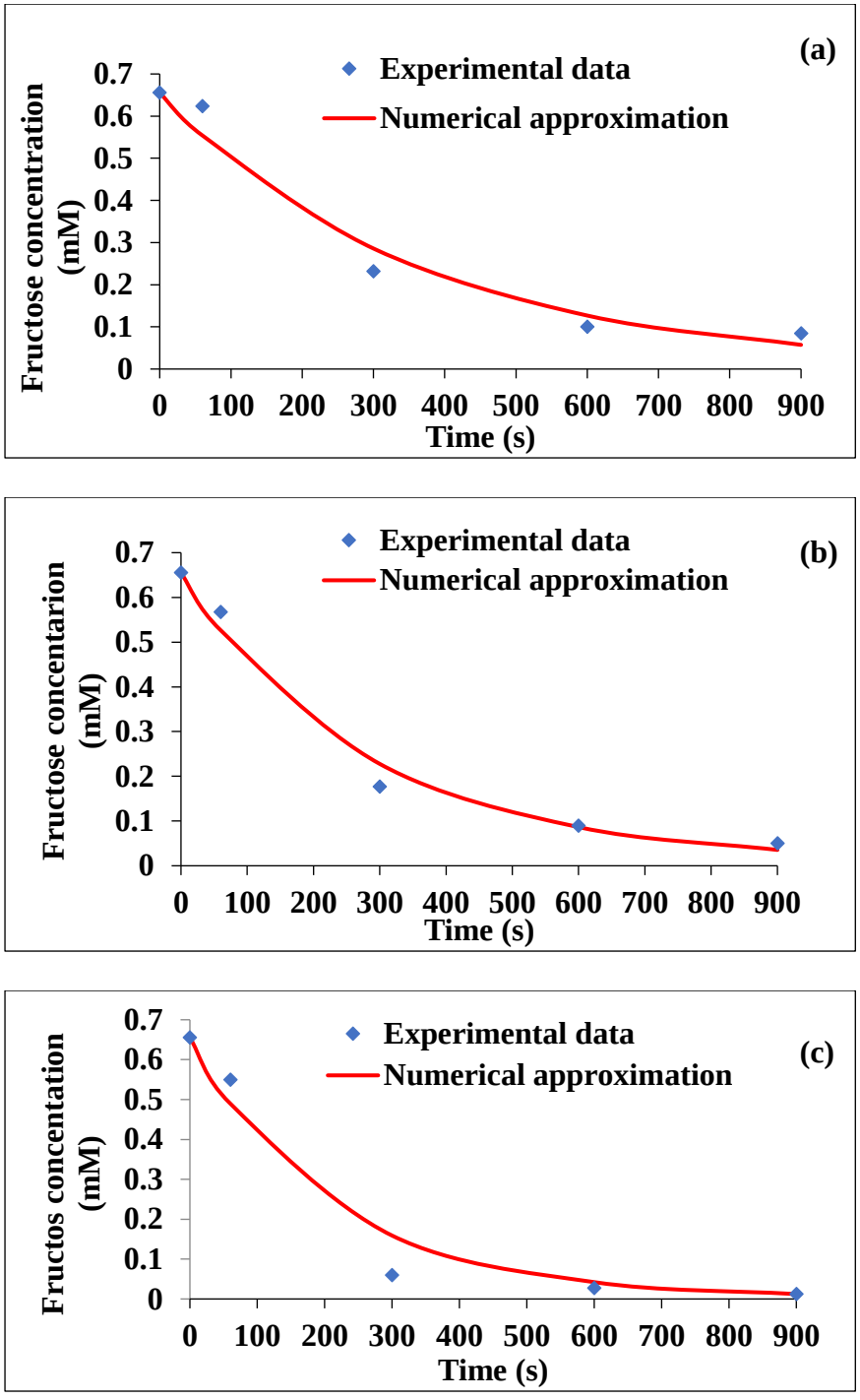


Figure 7.1. Experimental and numerical approximation data for DES1 at 60 °C (a), 70 °C (b) and 80 °C (c) fitted with (n) order rate equation

To determine the activation energy and frequency factor (A) for the fructose dehydration reaction using DES1, the natural logarithm of k values at the different

experimental temperatures are plotted versus the inverse of temperature (1/T) using Equation (7-6), as shown in Figure 7.2.

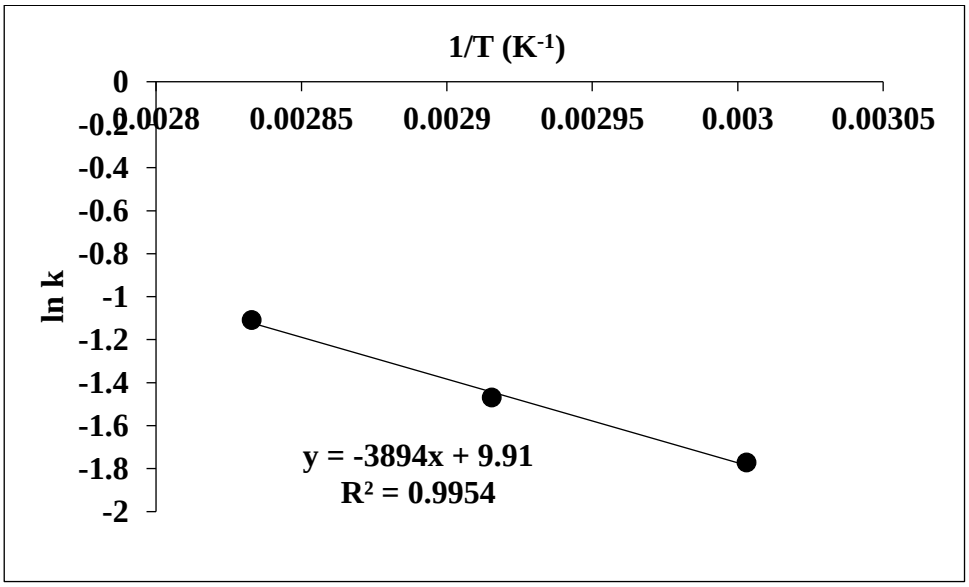


Figure 7.2. Estimation of activation energy and Arrhenius coefficient (frequency factor) for DES1

The activation energy (Ea) and frequency factor (A) are 32.37 kJ.mol^{-1} and 20×10^3 s^{-1}, respectively. This implies that the minimum energy necessary for the dehydration reaction of fructose to occur using DES1 is 32.37 kJ.mol^{-1}. This is the minimum energy required to activate the molecules to initiate a chemical reaction using DES1, while the number of collisions occurring during the reaction is 2×10^4 per second.

7.4.2 Reaction Kinetics of Fructose Dehydration in DES2

The (n) values obtained from the results illustrated in Figure 7.3 show clearly the first order depiction of the kinetic data obtained for DES2 for 60, 70 and 80 °C, respectively.

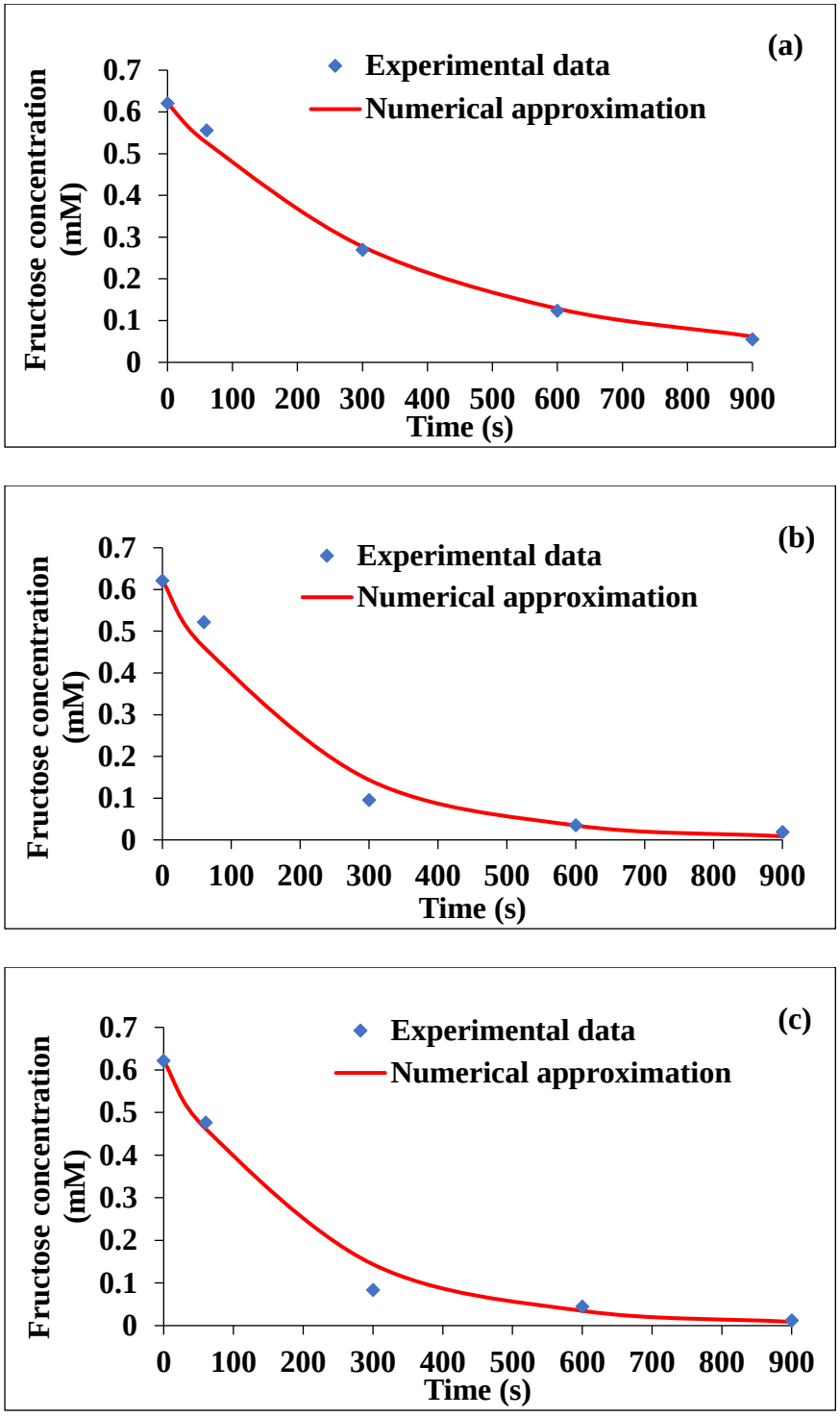


Figure 7.3. Experimental and numerical approximation data for DES2 at 60 °C (a), 70 °C (b) and 80 °C (c) fitted with (n) order rate equation

The rate constant (k) and reaction order (n) values are presented in Table 7.2.

Table 7.2. The k and n values of the fructose dehydration reaction using DES2 at different temperatures

Temperature °C	Reaction rate constant (k) s^{-1}	Reaction order (n)
60	2.83×10^{-3}	1.1
70	5×10^{-3}	1.0
80	5.5×10^{-3}	1.0

Again, the rate of reaction increases as the reaction temperature increases. Notably, the rate of reaction at 70 and 80 °C is approximately the same, which is consistent with the result reported in section 5.3.3 for DES2 on the effect of the reaction temperature. While DES1 and DES2 differed in their salt component, namely ChCl in DES1 and DEAC in DES2, the reaction order (first order) was found to be the same under the same experimental conditions, showing that the salt component did not affect the order of the reaction.

Figure 7.4 shows the plot of the rate constant fitted with the Arrhenius equation for DES2. Using Equation (7-6), the activation energy (Ea) of the fructose dehydration reaction and its frequency factor (A) were obtained from the slope and the intercept of plotting ln k versus 1/T. The activation energy and frequency factor are 32.63 $kJ.mol^{-1}$ and 24×10^{3} s^{-1}, respectively.

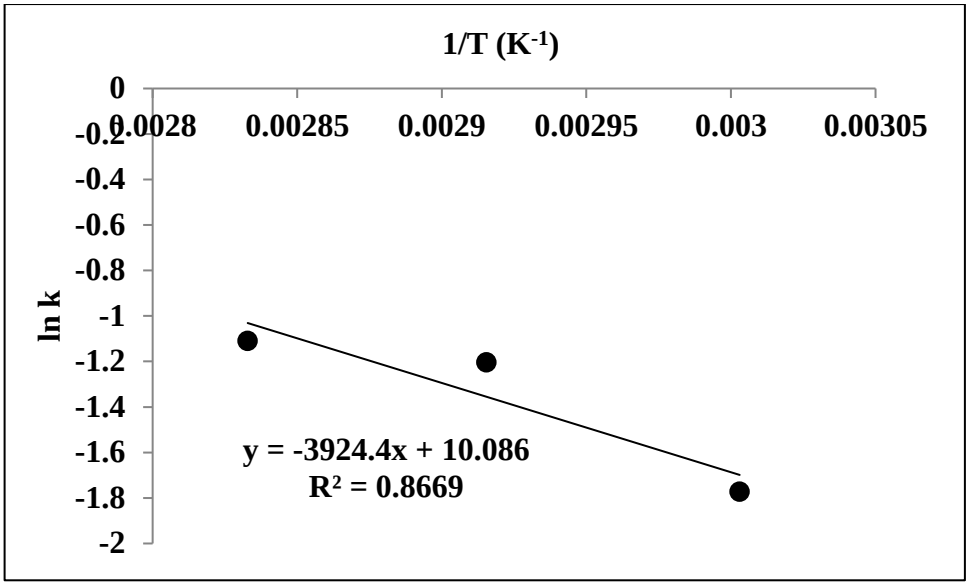


Figure 7.4. Estimation of activation energy and Arrhenius coefficient (frequency factor) for DES2

7.4.3 Reaction Kinetics of Fructose Dehydration in DES3

Using a similar procedure as above and Equation (7-2), the kinetics of the fructose dehydration reactions at 80, 90 and 100 °C using DES3 were studied. It was found that the reaction order was close to 1.8 for the three studied temperatures. The reaction rate constant (k) and reaction order (n) values obtained from the plots in Figure 7.5 using DES3 at 80, 90, and 100 °C are listed in Table 7.3.

Table 7.3. The k and n values for the dehydration reaction of fructose using DES3

Temperature °C	Reaction rate constant (k) $mol^{-0.8}\ L^{0.8}\ s^{-1}$	Reaction order (n)
80	2.83×10^{-3}	1.7
90	13.3×10^{-3}	1.8
100	30×10^{-3}	1.8

In contrast to DES1 and DES2, the reaction order is close to 1.8, as described by (n) values, and the rate constant (k) is temperature dependent, where the k values increase as the reaction temperature increases, which is consistent with the results presented in Figure 7.5. This implies that the kinetic energy of the molecules increases as well as the collision frequency, as the temperature increases. Hence, the dehydration of fructose increases with an increase in reaction temperature. It is also clear from Figure 7.5 that both the experimental and numerical approximation data did not fit well at the reaction temperature of 80 °C. This could be attributed to the low temperature used (80 °C) that is less than the melting point of the DES3 (85 °C), which led to a highly viscous reaction medium and slowed the reaction rate. The substituting of adipic acid in DES3 with the p-TSA acid in DES1 shifted the reaction order close to 1.8. However, in most of the literature, the dehydration of fructose is described by first order reaction kinetics, which differs from the 1.8 obtained in this study. This can be attributed to the bifunctional role of the DES, unlike the aqueous systems (solvent and acid) commonly reported in the literature.

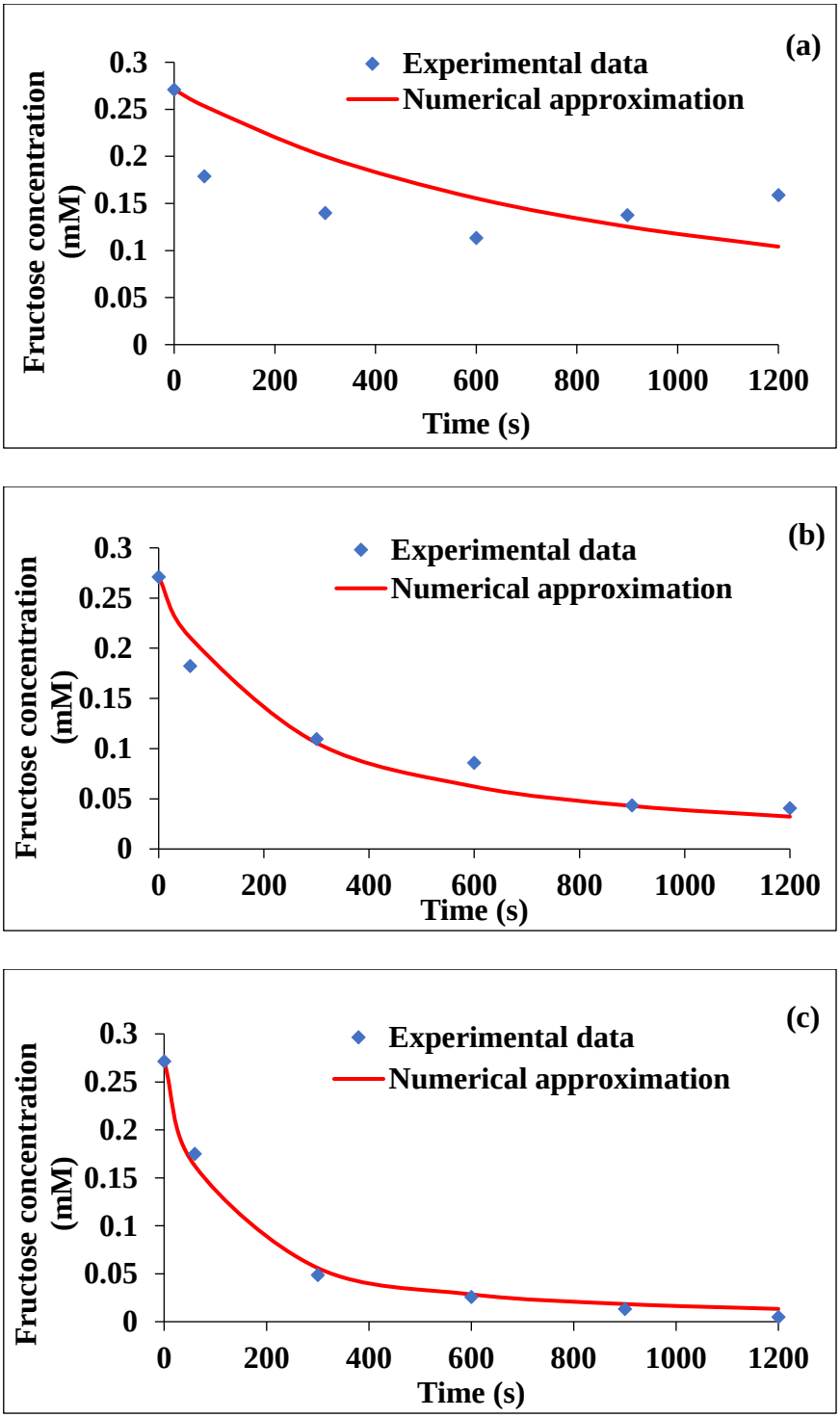


Figure 7.5. Experimental and numerical approximation data for DES3 at 80 °C (a), 90 °C (b) and 100 °C (c) fitted with (n) order rate equation

Using the Arrhenius equation, Figure 7.6 shows the effect of the reaction temperature on the kinetics of the dehydration of fructose using DES3. The activation energy and frequency factor (A) are 129.5 kJ.mol^{-1} and 2.76×10^{18} s^{-1}, respectively.

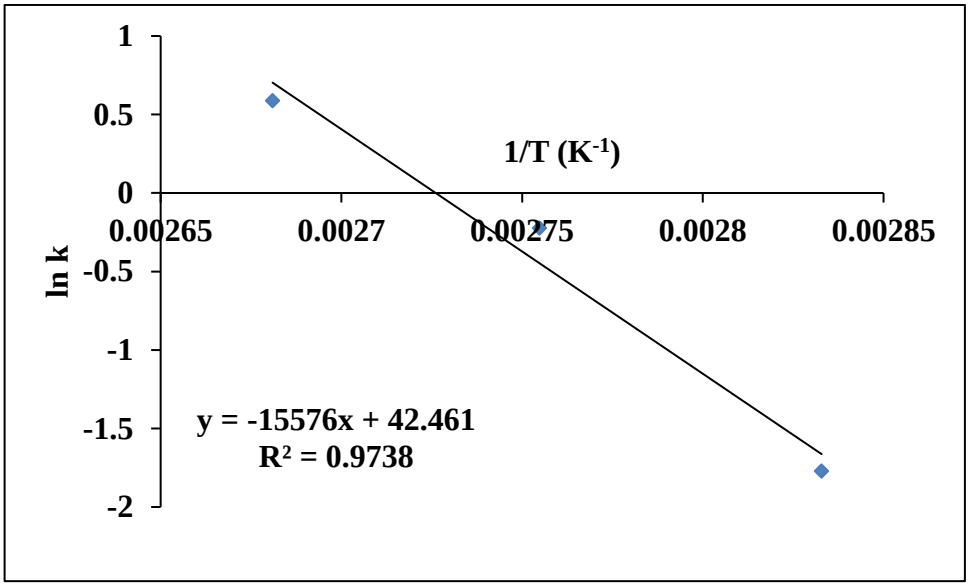


Figure 7.6. Estimation of activation energy and Arrhenius coefficient (frequency factor) for DES3

The activation energy required for DES3 is higher than the 93 kJ.mol^{-1} used for DES1. This is the reason for the higher reaction temperature necessary to initiate the chemical conversion upon the use of DES3, as reported in Chapter Six.

7.5 Discussion

The energy requirement for the dehydration of fructose to 5HMF by the DESs can be summarised as follows: DES1≈DES2<DES3, as shown in Table 7.4, which is consistent with Chapters 4, 5 and 6, respectively.

Table 7.4. Summary of the activation energy and frequency factor for the three DES systems

DES system	Activation energy ($kJ.mol^{-1}$)	Frequency factor (s^{-1})
DES1	32.37	20×103
DES2	32.63	24×10^{3}
DES3	129.5	2.75×10^{18}

The kinetics data approximated with nth order equation show clearly that the experimental data points for DES1 and DES2 can be approximated by a first order kinetic ("n" close to 1, for all the data shown in Figure 7-1 and Figure 7-3), while the reaction order is close to 1.8 for DES3. This means that the reaction pathway may be different from one DES to another, with this assumption being well correlated with the activation energy, which is similar for DES1 and DES2, while it is higher for DES3 (with a different acid component).

The different reaction pathway with DES3 could be due to an intermediate, which may be produced due to a different DES composition used and the higher activation energy required to initiate the reaction. This assumption is in agreement with the results reported by Kobayashi et al. (2015) for the reaction of fructose to 5HMF using ChCl/citric acid and ethyl acetate as a solvent at 70 – 120 °C and 0 – 240 min reaction time. They found that the reaction went through an intermediate, and that the order for the reaction from fructose to the intermediate was first order with an activation energy of 110 $kJ.mol^{-1}$, but later deviated from the first order as the reaction proceeded from intermediate to 5HMF. The ChCl/citric acid used in their study is of the same family as the DES3 (ChCl/adipic acid) used in this study. Although the acid components of the DES are different, the activation energies obtained are in a similar range: 110 vs 129.5 $kJ.mol^{-1}$. On

the other hand, the reaction orders are different: 1 vs 1.8. This difference in the order of reaction can be attributed to the composition differences in the DES and the additional solvent used by Kobayashi and co-workers (2015). By changing the acid component, the activation energy for DES1 was greatly lowered to 32.37 $kJ.mol^{-1}$ compared to that measured for DES3. Also, with DES1 the order of reaction was close to first order compared to being close to 1.8 for DES3.

The dehydration of fructose to 5HMF by DES2 (DEAC/p-TSA) was found to be close to first order reaction kinetics, which is similar to DES1 and consistent with the orders commonly reported in the literature (Chen et al., 2014a; Kobayashi et al., 2015; Xu et al., 2015a; Song et al., 2016). Despite the different salt used for DES2, the activation energies achieved using DES1 and DES2 were similar at 32.37 and 32.63 $kJ.mol^{-1}$, respectively. This may be because the same acid was used in both DES1 and DES2, which clearly shows that the reaction kinetics are affected by the acid component of the DES, which acts as a catalyst for the dehydration reaction. The activation energies obtained by the three DES systems were found to be within the range reported in the literature for other systems, where the lowest activation energy was 27.7 $kJ.mol^{-1}$ (80 – 160 °C), as reported by Song et al. (2016), and the highest was 165 $kJ.mol^{-1}$ (80 – 120 °C), reported by (Wei et al., 2011). In this study, the used DES performed the dual function of catalyst and solvent, while those reported in the literature used catalysts in addition to external solvents. The catalyst and external solvents have the potential to modify reaction pathways, which in turn influences the activation energies of the dehydration reaction of fructose to 5HMF. It is worth mentioning that no two studies in the literature have reported the same activation energies, because of the differences in catalyst and solvent used. Comparing the results obtained from the three DES systems used with the results reported in the literature, it is

clear that these systems have a high capability to efficiently reduce the activation energy and increase the fructose conversion rates at milder reaction conditions.

7.6 Conclusions

Kinetic studies of the fructose dehydration to 5HMF were carried out using formulated novel DESs, which are embedded with catalytic and solvent functions. The kinetics study was carried out at temperatures of 60, 70 and 80 °C for DES1 and DES2, and 80, 90 and 100 °C for DES3, at reaction time interval of 5 min from 0 – 20 min. It was found that DES1 and DES2 were close to first order reaction kinetics, while DES3 was close to a 1.8 order reaction pathway. The achieved activation energies obtained can be summarised in the following order: DES1 (32.37 $kJ.mol^{-1}$)≈DES2 (32.63 $kJ.mol^{-1}$)<DES3 (129.5 $kJ.mol^{-1}$). The energy requirement also followed the same order. This explains why the optimum reaction temperature for DES3 was higher than for DES1 and DES2, which shows that the composition of the DES greatly influences the activation energy.

Chapter 8 Comparison of the Studied DES Systems

8.1 Overview

Different DES formulations were prepared and tested, as described in Chapters Four, Five and Six. The compositions of the formulated DES are thus: ChCl and p-TSA (DES), DEAC and p-TSA (salt-modified DES) and ChCl and adipic acid (acid-modified DES). For the purpose of this chapter, the following nomenclatures will be used: DES1 (DES used in Chapter Four), DES2 (salt-modified DES used in Chapter Five) and DES3 (acid-modified DES used in Chapter Six). In Chapters Four, Five and Six, it was found that the composition of the DES influenced the optimum 5HMF yields and selectivity, as well as the experimental conditions. In this chapter, a detailed comparison between the three DES systems is presented and discussed.

8.2 The DES Systems Used

The increasing concerns about the non-green nature of organic synthesis processes and their environmental side effects have been discussed, with the aim of identifying the green chemistry constituents needed to create a green production process (Khandelwal et al., 2016). In general, green solvents should be low cost, easy to prepare, non-volatile, environmentally friendly, have thermal and chemical stability, be non-toxic and readily available (Liu et al., 2014). The selection of a green reaction medium remains the main challenge. The non-green reaction media such as aqueous systems (mineral acids and water) and organic solvents used in the dehydration of sugars to 5HMF still pose a problem in developing these systems.

In relation to this, the unique advantages of DES solvents such as their environmental compatibility, ease of preparation, low cost and the fact that they are renewable resources, have led to great interest in studying these solvents in organic

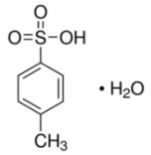
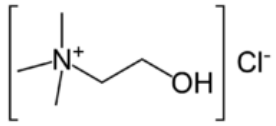
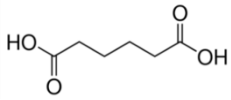
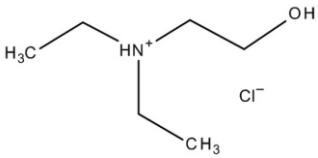
synthesis (Smith et al., 2014). Generally, the DES systems are characterised by their freezing points, which depend on the DES molar mixing ratios (Craveiro et al., 2016) and the nature of the two components. Despite the widespread use of DES solvents in many applications, the lack of studies on their properties and their effect on their applications remain weak points in the literature (Siongco et al., 2013).

In this chapter, the three different novel DES systems which are referred to as DES1, DES2 and DES3, which were used as reaction media for the dehydration of fructose to 5HMF, will be evaluated in terms of the fructose conversion, 5HMF yield and selectivity, and operating conditions. The properties and compositions of the formulated DES are summarised in Table 8.1. The chemical and molecular formulas of the acids and salts used, as well as their molecular weights, are presented in Table 8.2 (the data are adopted from the supplier's Material Safety Data Sheet (MSDS)).

Table 8.1. Properties of the studied DES systems

System	DES composition		DES molar mixing ratio (acid-to-salt)	Melting point (°C)		DES freezing/melting point (°C)	DES viscosity (Pa. s)	DES density (g/cm^3)	Reference
	Salt	Acid		Salt	Acid				
DES1	ChCl	p-TSA	(1:1)	302	103.5	2.7	0.183	1.207	(Zhao et al., 2015)
DES2	DEAC	p-TSA	(1:3)	133-136	103.5	38-45	-	-	(Hayyan et al., 2013)
DES3	ChCl	Adipic acid	(1:1)	302	153	85	-	-	(Abbott et al., 2004)

Table 8.2. The molecular formulas and molecular mass of the studied DESs' components

Acid	BP (°C)	Molecular formula	Molar mass (g/mol)	Salt	Molecular formula	Molar mass (g/mol)
p-toluensulfonic acid	140		172.2	Choline chloride		139.62
Adipic acid	337.5		146.14	N,N-diethylethanolammonium chloride		153.65

8.3 DES Formulations

The three DES systems used for the dehydration of fructose showed different reaction behaviours. In the formulation of these DESs, different characteristics were exhibited. During the preparation of DES1, for example, it was observed that it readily and completely mixed together and converted into a liquid form at room temperature within 60 min and without agitation. On the other hand, DES2 took a longer time (over 150 min) to partially mix at room temperature, while DES3 did not mix at all at room temperature, even when left overnight. This clearly shows that the nature of the DES materials and their mixing ratios are important factors in DES preparation, which could lead to different freezing points, as shown in Table 8.1.

During the heating and mixing of the DES mixtures, it was observed that DES1 was completely converted to liquid when heated at 80 °C and 300 rpm for 20 min. DES2 was converted to liquid after 35 min at the same heating temperature and agitation speed. DES3 showed a completely different behaviour in that it required a higher temperature (90 °C) and longer time (60 min) to mix.

The best experimental conditions achieved with the different DES formulations are presented in Table 8.3. Figure 8.1 displays the fructose conversions, 5HMF yields and selectivity at the achieved optimum conditions presented in Table 8.3. It is clear from Table 8.3 that the acid-modified DES (DES3) required a higher reaction temperature and longer reaction time to achieve a higher 5HMF yield and selectivity compared to DES1 and DES2. . The 90 °C and 120 min required for DES3 against 80 °C and 60 min needed by DES1 can be attributed to the high melting point of DES3. Consequently, using DES3 resulted in 100% fructose conversion compared to approximately 84.5% obtained with DES1. This represents 15.5% higher conversion with DES3; as a consequence, the 5HMF

yield and selectivity upon the use of DES3 are also higher than DES2, despite the higher yield achieved by DES3, the selectivity of DES1 is slightly higher than DES3. This shows that DES3 outperformed DES1 and DES2, however, DES3 requires 10 °C higher reaction temperature than DES 1 and DES2. This temperature could have promoted some side reactions that suppressed the 5HMF yield, despite the 100% conversion achieved (Figure 8.1). The side reactions could have been activated also by longer time required by DES3 (Table 8.3).

Table 8.3. The highest 5HMF yields obtained from the three studied DES systems and their reaction conditions

DES system	Temp. (°C)	Time (min)	DES mix. Ratio (salt-to-acid)	Feed mass ratio	Fructose conversion mol%	5HMF yield mol%	5HMF selectivity mol%
DES1	80	60	1.5:1	5	84.5	78.3	92.6
DES2	80	60	0.5:1	5	88.6	84.8	88.6
DES3	90	120	1:1	2.5	100	90.8	90.8

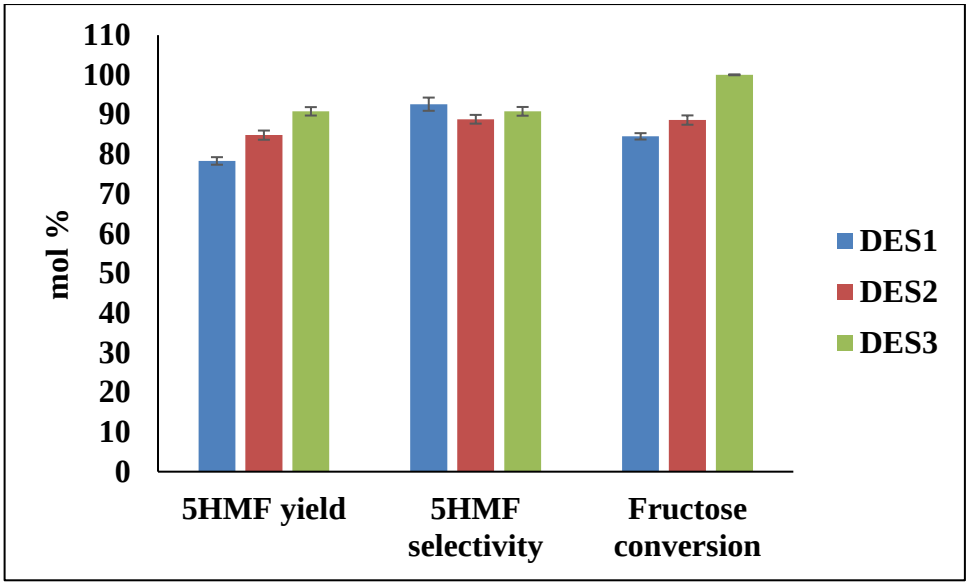


Figure 8.1. The highest 5HMF yields and their conversion and selectivity obtained from the studied DES systems

Comparing DES1 and DES2, an additional 4.1% fructose conversion was achieved using DES2 at the same reaction temperature and time (Table 8.3 and Figure 8.1). Despite the higher fructose conversion observed by using DES2, the 5HMF yield is 6.5% more than the 78.3% obtained for using DES1, in contrast the selectivity of DES1 is 4% higher than that achieved with DES2 (Table 8.3). This implies that for DES1, a high fructose conversion does not lead to a higher 5HMF yield. This could be due to the activation of side reactions by DES1 compared to DES2 in spite of the reaction temperature and feed ratio been the same. However, with DES2 a lower molar mixing ratio (acid-to-salt) was used compared to DES1. Overall, with DES3 100% fructose conversion can be achieved compared to DES1 and DES2. The higher temperature and longer time may have contributed to achieving this complete fructose conversion (Table 8.3). Conversely, the higher conversion achieved with DES2 compared to DES1 could be attributed to the role played by the different salts used, which may have influenced the interaction and promoted

the donation of proton necessary to enhance the dehydration reaction. The molar mixing ratios within the DES can also influence the extent of this interaction (Table 8.3).

8.4 Conversion, Yield, and Selectivity

In the following subsections, the formulated DES1, DES2 and DES3 are evaluated based on the effect of feed ratio, reaction time, reaction temperature and molar mixing ratio, respectively, on the fructose conversion, 5HMF yield and selectivity achieved.

8.4.1 Feed Ratio

The influence of feed ratio (fructose-to-DES) on fructose conversion (a), 5HMF yield (b) and 5HMF selectivity (c) upon the use of DES1, DES2 and DES3 are presented in Figure 8.2a – c. In terms of conversion (Figure 8.2a), it is clear that at lower feed ratio in the range of 2.5 to 10, the fructose conversion follows the order DES3 > DES2 > DES1, with DES3 achieving a significant conversion of 100% at a feed ratio of 2.5. At a feed ratio of 20 the order changes to DES3 > DES1 > DES2, and for a feed ratio range of 30 to 100 the fructose conversion achieved by DES1 and DES2 are approximately the same. However, with DES1 the conversion increases with the feed ratio from 2.5 to 30, and thereafter remains constant, while for DES2 the fructose conversion is independent of the feed ratio in the range of 5 to 100. Notably, DES1 and DES2 have the same acid component (p-TSA) and different organic salt components (DES1 – ChCl, DES2 – DEAC); however, the difference in compositions showed little or no effect on the fructose conversion as the feed ratio increased from 20 to 100.

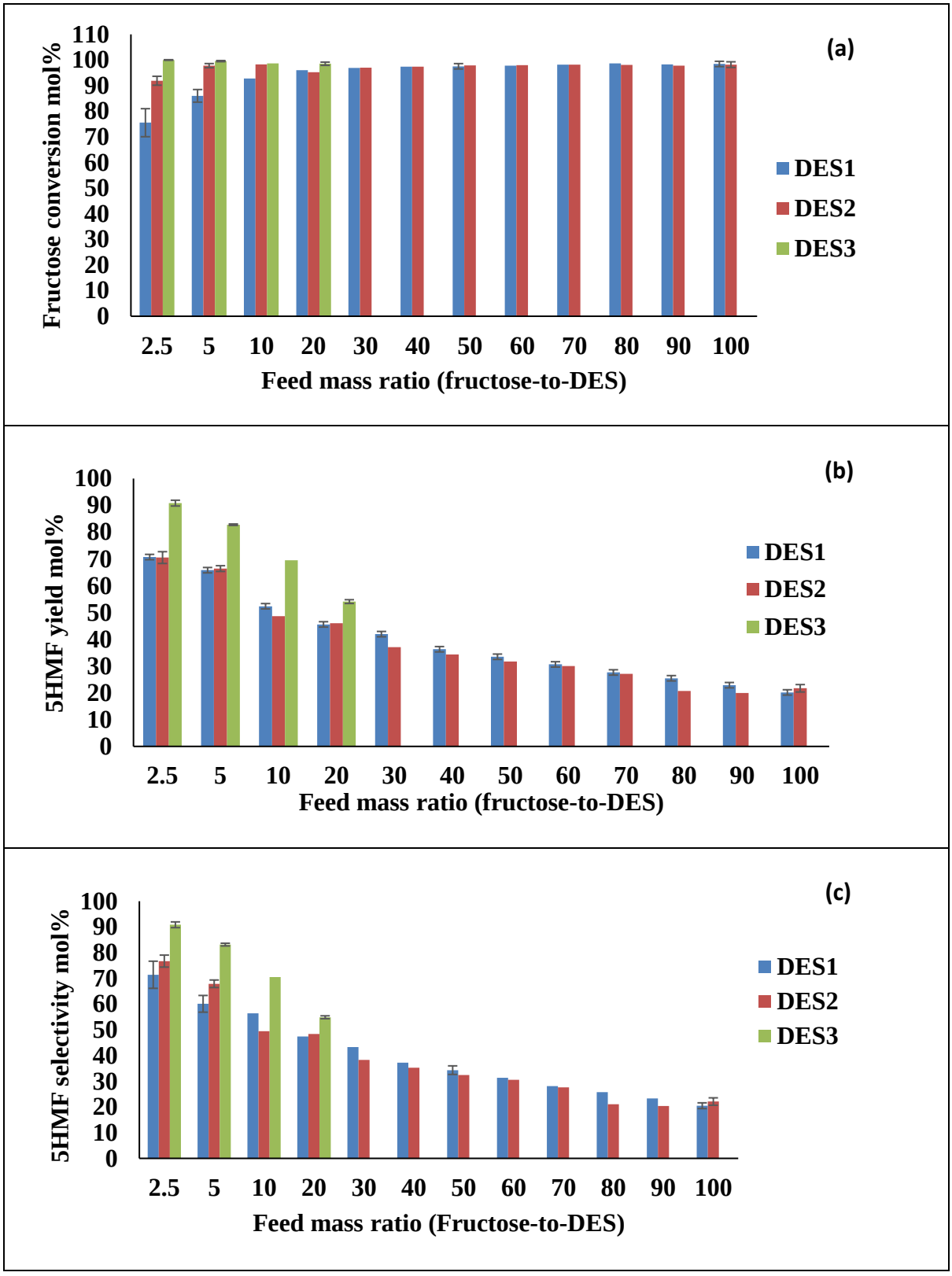


Figure 8.2. The effect of feed ratio (fructose-to-DES) on fructose conversion (a), 5HMF yield (b) and selectivity (c)

At a feed ratio of 2.5, DES1 and DES2 gave similar 5HMF yields of approximately 71%, which is approximately 20% less than that achieved with the use of DES3 (Figure 8.2b). DES3 showed high 5HMF yields compared to DES1 and DES2 for the feed ratio range of 2.5 to 20. This is consistent with the fructose conversion presented in Figure 8.3a and is attributed to the higher reaction temperature and longer time necessary to achieve the optimum 5HMF yield compared to DES1 and DES2. On the other hand, DES1 and DES2 showed a similar trend, decreasing with increasing feed ratio. However, the 5HMF yield for DES1 was slightly higher than that of DES2 as the feed ratio increased from 10 to 90 except 2.5-10. Convincingly, DES1 outperformed DES2 for the range of feed ratio studied in terms of the 5HMF yields. Despite the similarity in the optimum conditions between DES1 and DES2, some slight differences can be noticed (Figure 8.2a – c), which could be due to the different salts used for the two DES systems.

The effect of the DES composition on the 5HMF selectivity as a function of the feed ratio is shown in Figure 8.2c. Comparing Figure 8.2b and 8.2c, it is clear that the 5HMF selectivity follows a similar trend to the yield. However, at a feed ratio of 2.5 DES3 showed a higher selectivity than DES1 and DES2 (DES2 > DES1), whereas their yields were similar at the same feed ratio (Figure 8.2b and 8.2c). This difference can be attributed to the roles of the p-TSA and adipic acids used, since they both have the same organic salt (ChCl). While p-TSA is known to be a strong Brønsted acid, adipic acid is considered a weak dicarboxylic acid. This could influence the molecular level interaction during the dehydration reaction, and especially the protonation of the hydroxyl group in the fructose ring. This clearly shows that the composition of the DES is a key factor for the selection of the optimum conditions of the dehydration reaction of fructose to 5HMF.

8.4.2 Reaction Time

The different DES systems are evaluated here as a function of the reaction time. Figure 8.3a – c shows the performance of DES1, DES2 and DES3 for the range of reaction times investigated. Regarding the conversion of fructose, DES1 is slightly higher than DES2 for the reaction time range of 10 to 90 min. Notably, for the longer reaction time of 100 – 110 min, DES2 slightly outperformed DES1. It is not clear what is responsible for this; however, it is well known that a longer reaction time would result in a higher conversion. On the other hand, at reaction times of 30, 60, 90 and 120 min, DES3 showed a higher fructose conversion compared to DES1 and DES2. Since all the other factors are the same, the only factor that could contribute to this performance is the higher reaction temperature of 90 °C used for DES3, compared to 80 °C used in DES1 and DES2.

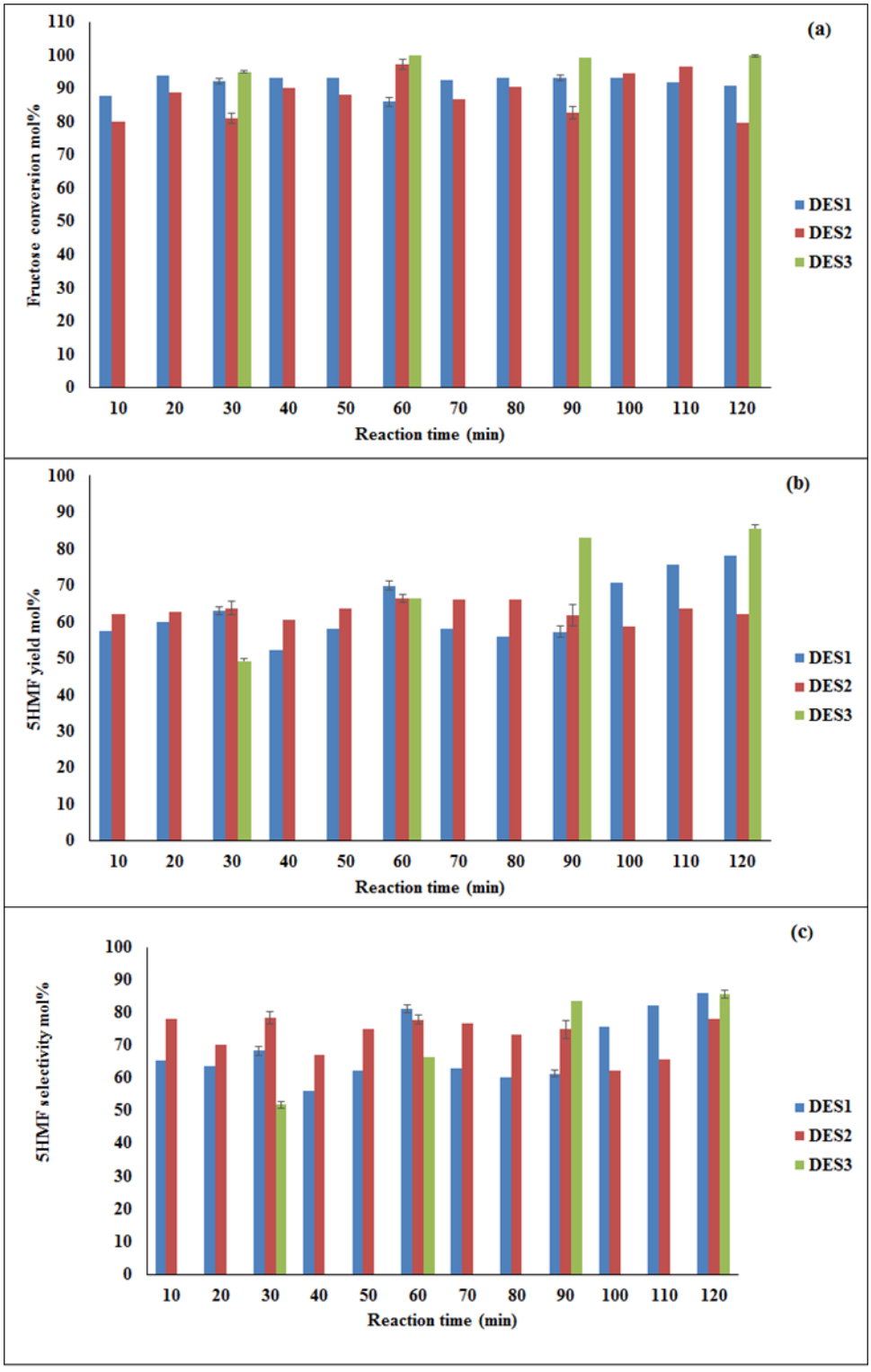


Figure 8.3. The effect of reaction time on fructose conversion (a), 5HMF yield (b) and 5HMF selectivity (c)

It is believed that higher conversion would correspond to higher yield. Despite DES1 having slightly higher conversion than DES2 for the time range 10 – 50 min, the corresponding 5HMF yield, however, revealed that DES2 achieved slightly higher yields than DES1 for the same time range (Figure 8.3a and 8.3b). This implies that within this time range, more side reactions which inhibit the reaction that leads to the formation of 5HMF have taken place with DES1 than DES2. This can be attributed to the difference in the interactions resulting from a change in the salt from ChCl salt in DES1 to DEAC organic salt in DES2. Beyond the 50 min reaction time, fluctuation can be noticed in the yield between DES1 and DES2. Similarly, DES3 showed a higher fructose conversion at reaction times of 30, 60 and 90 min, but the corresponding 5HMF yields obtained were low except at 90 min, where higher conversion gave higher yield. Therefore, DES3 performs better at the longer reaction time, which is expected because of its high melting point.

In terms of selectivity (Figure 8.3c), it can be observed that DES2 showed higher 5HMF selectivity than DES1 in the reaction time range of 10 to 90 min, except for 60 min (DES1 > DES2). Since both DESs have the same acid component (p-TSA), it follows that the presence of DEAC in DES2 compared to ChCl used in DES1 could have promoted the reaction route, leading to the production of 5HMF. This reaffirmed the 5HMF yields observed in Figure 8.3b for DES2 against DES1, and validates the notion of side reaction occurrence, which has been reported in the literature. At lower reaction times of 30 and 60 min, DES3 showed low 5HMF selectivity compared to DES1, while at higher reaction times such as 90 min and above its selectivity increased significantly. This could be attributed to the differences in the properties of the acids used in DES1 (p-TSA) and DES3 (adipic), and their interaction with the ChCl salt.

8.4.3 Reaction Temperature

The effect of reaction temperature and DES composition on fructose conversion, 5HMF yield and selectivity is presented in Figure 8.4a – c. As expected, fructose conversion increases with reaction temperature for the three DES systems. The increasing thermal energy increases the rate of reaction. A similar fructose conversion can be noticed for the three DES systems at the optimum reaction temperature achieved for DES1 and DES2. Despite a fructose conversion of around 90% obtained at 80 °C for the three DES systems (Figure 8.4b), the 5HMF yields are in the order DES1 > DES2 > DES3 at the same temperature. This difference can be attributed to the composition of the DES systems. Since DES1 and DES2 have the same acid (p-TSA) but different salt (DES1 – ChCl, DES2 – DEAC), this means that the ChCl in DES1 could have promoted the pathway that leads to the production of 5HMF while suppressing other side reactions, compared to DES2 at reaction temperature 80 °C. This can be confirmed from the results for other reaction temperatures except 100 °C, where DES1 and DES2 showed approximately the same 5HMF yield of 51%.

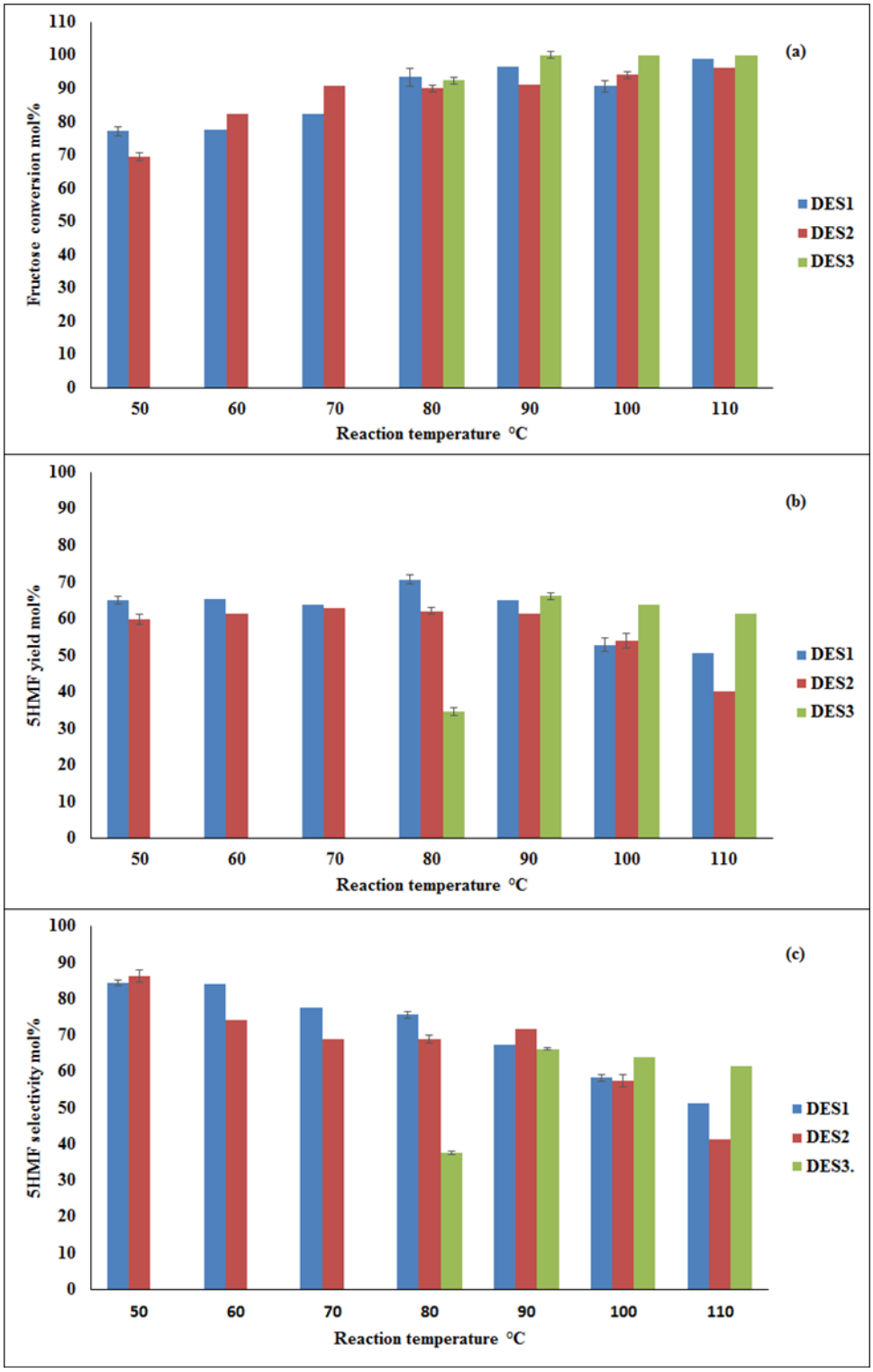


Figure 8.4. The effect of reaction temperature on fructose conversion (a), 5HMF yield (b) and 5HMF selectivity (c)

At the same time, when comparing DES1 and DES3 at 80 °C, while both DES systems gave the same conversion, the 5HMF yield was higher for DES1 due to the presence of p-TSA acid compared to DES3, which contains adipic acid. The reason for the lower 5HMF yield for DES2 and DES3 is because of the side reactions occurring. These observations were reinforced in the 5HMF selectivity for the three DES systems presented in Figure 8.4c. At this point it should be noted that no fructose conversion, 5HMF yield or selectivity was recorded for DES3 for reaction temperatures below 80 °C. The high melting point of DES3 and its weak dicarboxylic acid content require a high temperature to enhance the kinetic energy of the molecules to initiate reaction. Hence, DES3 showed a higher performance at reaction temperatures greater than 80 °C compared to DES1 and DES2. Moreover, the three DES systems showed decreasing 5HMF yield and selectivity from a reaction temperature of 90 °C and above (Figures 8.4b and 8.4c). This is because of the increasing effect of side reactions with increasing reaction temperature.

8.4.4 DES Mixing Ratio

Figure 8.5a – c shows the fructose conversion, 5HMF yield and selection, respectively, as a function of the DES composition and DES molar mixing ratio. It is clear that DES2 gave a fructose conversion of approximately 1.5% higher than that obtained for DES1 for the molar mixing ratio of 0.5:1 to 2:1 (Figure 8.5a). Despite the difference in the composition of DES1 and DES2, it can be observed that the molar mixing ratio (acid-to-salt), in contrast to the reaction time, temperature, and feed ratio, does not have a great influence on the fructose conversion. With DES3, a slightly higher conversion can be noticed from mixing ratio 0.5:1 to 1.5:1, but at mixing ratio 2:1 the conversion level drops. This observation has been previously explained in Chapters Four and Five, and section 8.4.3.

In the mixing ratio studied, the 5HMF yield for DES2 decreases while that for DES1 increases from 0.5:1 to 1.5:1, before decreasing at 2:1. For the DES1 system, the 5HMF yield increased by 25.3% from 53 to 78.3% as the acid ratio increased from 0.5:1 to 1.5:1, after which the yield decreased by approximately 49% when the acid ratio increased to 2:1. For DES2 a near 61% decrease in 5HMF yield was observed from a molar mixing ratio of 0.5:1 to 2:1. This implies that for DES2, the decreasing amount of salt component (DEAC) significantly decreases the activity and performance, while for DES1 the opposite can be observed for ChCl, except at 2:1 (molar mixing ratio). A similar trend can be seen for the 5HMF selectivity presented in Figure 8.5c. In a similar way, the selectivity increased by 32% as the acid ratio increased from 0.5:1 to 1.5:1 and decreased by approximately 59% when the molar mixing ratio was further increased to 2:1 for DES1. On the other hand, DES2 experienced a progressive decrease in 5HMF selectivity from 85 to 21% for the same mixing ratio. This could be attributed to the different ionic interaction between the salt and the acid used in DES1 and DES2 over different mixing ratios. Conversely, when the DES3 was used as a reaction medium, the dehydration reaction behaved differently in terms of the 5HMF yield and selectivity. These observations clearly show that the composition of the DES and the molar mixing ratios are important parameters in the dehydration reaction of fructose to 5HMF.

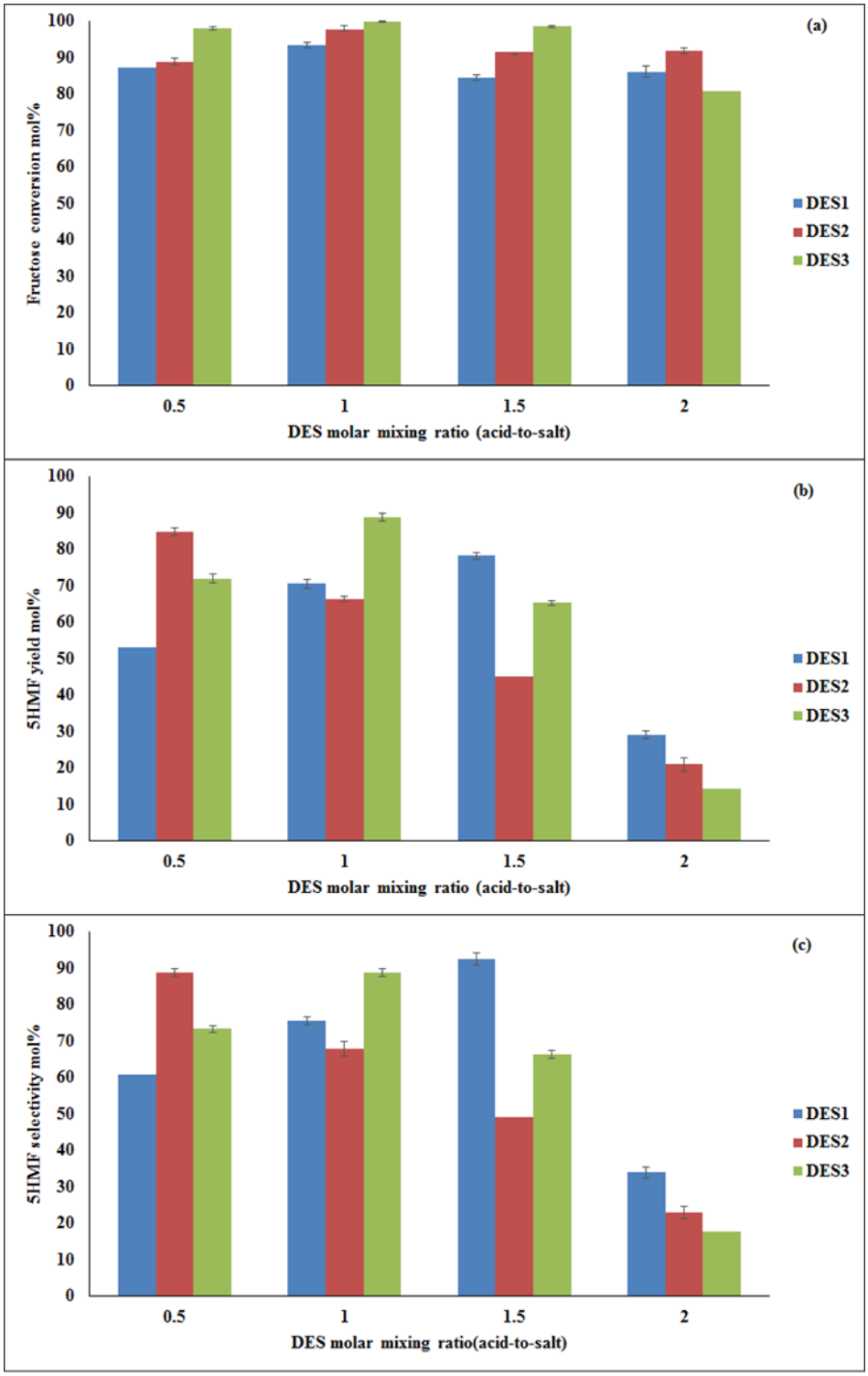


Figure 8.5. The effect of DES molar mixing ratio on fructose conversion (a), 5HMF yield (b) and 5HMF selectivity (c)

8.5 Conclusions

The three DES systems reported in Chapters Four, Five and Six were compared with the aim of understanding the effect of the different salt and acid components of each DES. The effect of DES composition was significant for the fructose conversion in the feed ratio of 2.5 – 10, but beyond this feed ratio the conversion was almost the same irrespective of the composition. However, the 5HMF yield and selectivity both decrease as the feed ratio (fructose-to-DES) increases from 2.5 to 100 for the three DES systems.

At 80 °C, the 5HMF yield for the three DES systems can be summarised as DES1 > DES2 > DES3. It was therefore found that the ChCl in DES1 promoted the yield of 5HMF compared to the DEAC salt used in the DES2 formulation. The p-TSA acid in DES1 contributed more in the 5HMF yield than the adipic acid used in the DES3 formulation at 80 °C. It was also found that the use of adipic acid in the formulation of DES3 required a higher reaction temperature, with the minimum being 80 °C to initiate the dehydration reaction of fructose to 5HMF, compared to DES1 and DES2. This is because of the higher melting point and weak adipic acid of DES3.

Chapter 9 Conclusions and Future Work

9.1 Overview

In this study, three novel Deep Eutectic Solvents (DESs) were formulated with a dual functionality as catalyst and solvent using p-TSA acid, ChCl salt, adipic acid, and DEAC salt. These DESs, namely DES1 (p-TSA and ChCl), DES2 or salt-modified DES (p-TSA and DEAC) and DES3 or acid-modified DES (adipic acid and ChCl), which have environmental and economic benefits as raw materials since their preparations are readily available and cheap, were tested in terms of the fructose dehydration reaction to 5HMF. The effect of the following ranges of experimental conditions were evaluated: temperature 50– 120 °C, time 5 – 180 min, feed mass ratio 2.5 – 100 (fructose-to-DES) and DES molar mixing ratio 0.5:1 – 2:1 (acid-to-salt) at an agitation speed of 300 rpm and atmospheric pressure. The performance of each DES was evaluated in terms of the 5HMF yields, selectivity, and fructose conversion as a function of the above-mentioned ranges of conditions. The reactions were carried out in an open batch reactor system using a magnetic stirrer and an oil bath as a heat transfer system. The effect of the DES composition on the optimum yield of 5HMF, selectivity and fructose conversion was examined. The chemical reaction kinetics of the fructose dehydration reaction to 5HMF using DESs as reaction media and catalyst were also studied and reported.

The DESs were produced from materials which are readily available and cheap, thus providing environmental and economic benefits. They were easy to prepare and had no contamination effect because they are not reactive. They performed a dual function by eliminating the need for a co-solvent, unlike expensive ionic liquids. No external catalyst was needed as the acid in the DESs served as both hydrogen bond donors (HBDs) and catalyst for the dehydration reaction of fructose. There was no need to add water, as the

DESs could dissolve fructose and led to high conversions. It was found that the use of DESs eliminated the rehydration effect experienced with aqueous systems, which greatly impeded 5HMF yields. The process achieved high 5HMF yields at mild conditions of temperature (80 and 90 °C) and pressure (1 atm) when compared to heterogeneous systems where severe conditions are required to achieve a similar yield.

9.2 DES1 Composed of ChCl and p-TSA

The effects of the feed ratio, reaction time, reaction temperature and DES mixing ratio were studied using DES1. It was found that the best conditions were temperature 80 °C, reaction time 60 min, feed ratio (fructose-to-DES) 5 and molar mixing ratio 1.5:1. The optimum 5HMF yield achieved at the best conditions was approximately 78.3%, with selectivity of 92.6% and fructose conversion 84.5%. Note that the optimum conditions are those that led to the highest 5HMF yield within the range of experimental conditions investigated, as increasing the productivity of 5HMF will benefit the economics of the process. Notably, the 5HMF yield and selectivity decreased when the initial fructose ratio was increased. However, it was observed that the dehydration reaction was much more reproducible in terms of the 5HMF yield and selectivity at a feed ratio of 5. The 5HMF yield and selectivity fluctuated within the reaction time studied, while the fructose conversion was almost constant (~90%) for the reaction time ranging from 10 to 120 min at 80 °C, feed ratio 5, and molar mixing ratio 1:1.

The effect of the reaction temperature showed that fructose conversion increases as temperature increases. The effect of the DES molar mixing ratio showed that the 5HMF yield and selectivity increased as the molar mixing ratio of the acid increased from 0.5 to 1.5, after which both the yield and selectivity sharply decreased. The fructose conversion,

however, was not greatly affected by increasing the DES molar mixing ratio as it remained constant at an average of 90%.

9.3 DES2 Composed of DEAC and p-TSA

DES2 (salt-modified DES) was prepared with DEAC and p-TSA. Similar to DES1, the effect of the four factors on the dehydration reaction was studied. It was found that the best conditions were temperature 80 °C, reaction time 60 min, feed ratio (fructose-to-DES) 5 and molar mixing ratio 0.5:1. The corresponding optimum 5HMF yield achieved at the best conditions was 84.8%, with selectivity of 88.6% and fructose conversion 88.6%. The effect of the feed ratio on the 5HMF yield and selectivity showed a similar trend to the one observed with DES1. However, the optimum feed ratio and molar mixing ratio for DES1 were different to DES2. The conversion of fructose was steady, as high as 98%, and was not influenced by increasing the feed ratio. The effect of the reaction temperature showed that fructose conversion increased as the temperature increased. Conversely, the 5HMF yield and selectivity decreased with increasing temperature.

In this system, the influence of changing the organic salt on the dehydration reaction was investigated. It was found that an increase in the yield of 5HMF of approximately 6.5% was observed with DES2 compared to DES1, while, the selectivity of DES1 was slightly higher than that of DES2, the fructose conversion with DES2 was approximately 4% more than DES1. This is as expected that the high conversion achieved with DES2 would give a higher yield of 5HMF compared with that achieved with DES1 at a lower conversion. This shows that the substituted salt (DEAC) in DES2 would have greatly influenced the reaction path, leading to the formation of 5HMF. The 5HMF yield and selectivity fluctuated less with increasing reaction time compared with the previous system. Both the 5HMF yield and selectivity decreased with the increasing molar mixing

ratio of DES2. The conversion of fructose was not influenced by changing the molar mixing ratio.

9.4 DES3 Composed of ChCl and Adipic Acid

DES3 (acid-modified DES) was formulated with ChCl and adipic acid. In this system, the influence of changing the HBD on the dehydration of fructose to 5HMF was investigated. It was found that with DES3, the dehydration of fructose to 5HMF required a higher reaction temperature and a longer reaction time compared to DES1. The best reaction conditions were found to be: temperature 90 °C, reaction time 120 min, feed ratio 2.5 (fructose-to-DES) and molar mixing ratio 1:1. The optimum 5HMF yield achieved at the best conditions was approximately 91%, with selectivity of 91% and fructose conversion of 100%. Despite, the use of similar salt (ChCl) in DES3 and DES1 the optimum molar mixing ratios were different (1:1) and (1.5:1) respectively, and the optimum 5HMF yields of DES3 was 6% higher than obtained when DES1 was used. The fructose conversion being 15.5% higher with DES3 relative to DES1. This major difference in fructose conversion can be attributed to the long reaction time and higher reaction temperature needed by the DES3 system due to the higher melting point of the formulated DES3, which results from the use of the weak adipic acid.

With DES3, an increase in reaction time beyond 150 min resulted in a decrease in 5HMF yield and selectivity, while the fructose conversion remained constant (100%) for reaction times above 150 min. It was also found that the dehydration of fructose to 5HMF using DES3 could only be initiated at temperature equal to or greater than 80 °C, compared to 50 °C for DES1. Hence, with DES3 there will be higher operating costs compared to DES1 to achieve the same 5HMF yield. The effect of the reaction time on the dehydration reaction using DES3 showed that both the 5HMF yield and selectivity

increased as the reaction time was increased from 30 to 120 min, after which time both decreased.

9.5 Kinetics of Fructose Dehydration Reactions in DES Systems

The kinetics of the fructose conversion to 5HMF using the formulated novel DESs with dual function capabilities (catalyst and solvent roles) were explored. It was found that the reaction order was highly influenced by the composition of the DESs. The dehydration reaction with DES1 was close to the first order. The values of the activation energy and the exponential factor for DES1 were 32.37 kJ mol^{-1} and 20×10^{3} s^{-1}, respectively. The rate constant values at the examined temperatures were $2.83\times10\text{-}^{3}$ s^{-1} (60 °C), 3.83×10^{-3} s^{-1} (70 °C) and 5×10^{-3} s^{-1} (80 °C), respectively. Similarly, for DES2 the experimental data were close to the first order, while the activation energy and exponential factor values of the reaction were 32.63 kJ mol^{-1} and 24×10^{4} s^{-1}, respectively. It was observed that the reaction rate constant slightly increased as the temperatures increased, thus 2.83×10^{-3} s^{-1} (60 °C), 5×10^{-3} s^{-1} (70 °C) and 5.5×10^{-3} s^{-1} (80 °C). A similar observation was recorded with DES3, where the rate constant increased from 2.83×10^{-3} to 13.3×10^{-3} and 30×10^{-3} $mol^{-0.8}$ $L^{0.8}$ s^{-1}, as the reaction temperature was increased from 80 to 90 and 100 °C, respectively. However, a reaction order close to 1.8 was found to describe the kinetics data obtained. The activation energy and exponential factor values using DES3 for the dehydration reaction were 129.5 kJ mol^{-1} and 2.76×10^{18} s^{-1}. These results revealed that the three DES systems promoted dehydration of fructose to 5HMF in an efficient and cost-effective manner, with a lower environmental footprint compared to systems using catalyst and solvent.

9.6 Future Work

Throughout this research, different areas regarding the use of DESs in the dehydration of fructose to 5HMF were found to be domains for further investigation or future work:

- The purification or the separation of 5HMF as a final product from the reaction mixture still needs further investigation in order to make the process more efficient.
- The study of the reusability of the DESs, as the high water solubility of both 5HMF and DESs poses a challenge in recovering the DESs. DES recovery would require a solvent extraction using an organic solvent to remove the 5HMF from the aqueous phase into the organic phase, a process which could not be done in this work due to the limitations of the analytical system used.
- The need to establish a continuous extraction of 5HMF during the process to eliminate the rehydration of 5HMF caused by the water produced from the reaction as a by-product.
- The need to establish a robust analytical technique to identify and quantify the possible by-products produced from the dehydration reactions, in order to better understand the fructose dehydration reaction behaviours with changing process parameters.

List of Author's Publications

Journal Publications

[1] Assanosi, A.A., Farah, M. M., Wood, J. and Al-Duri, B. (2014) 'A facile acidic choline chloride–p-TSA DES-catalysed dehydration of fructose to 5-Hydroxymethylfurfural'. *RSC Advances*, 4(74), pp. 39359-39364. DOI:10.1039/C4RA07065H.

[2] Assanosi, A., Farah, M. M., Wood, J. and Al-Duri, B. (2016) 'Fructose dehydration to 5HMF in a green self-catalysed DES composed of N, N-diethylethanolammonium chloride and p-toluenesulfonic acid monohydrate (p-TSA)'. *Comptes Rendus Chimie*, 19(4), pp. 450-456. DOI:10.1016/j.crci.2015.11.004.

[3] Assanosi, A., Wood, J. and Al-Duri, B. (2017) 'Dehydration of Fructose to 5-Hydroxymethylfurfural Applying a Novel Green Self-Catalysed Deep Eutectic Solvent'. (intended for publication).

Conference Paper

[1] Assanosi, A., Farah, M. M., Wood, J. and Al-Duri, B. (2015) 'Fructose dehydration to 5HMF in a green self-catalysed DES composed of N, N-diethylethanolammonium chloride and p-toluenesulfonic acid monohydrate (p-TSA)'. Proceeding of the 6th International Renewable Energy Congress, March 24 – 26th 2015, Sousse, Tunisia. Awarded the "Best Paper Award".

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Appendices

Appendix A: Experimental Sample Calculation Equations:

The 5HMF yield and selectivity, fructose conversion, feed mass ratio and DES molar mixing ratio were calculated using the following equations:

$$5HMF\ Yield\% = \left(\frac{moles\ of\ 5HMF\ produced}{initial\ moles\ of\ fructose}\right) \times 100 \quad \text{(A-1)}$$

$$5HMF\ Selectivity\% = \left(\frac{moles\ of\ 5HMF\ produced}{converted\ moles\ of\ fructose}\right) \times 100 \quad \text{(A-2)}$$

$$Fructose\ Conversion\% = \left(\frac{moles\ of\ fructose\ converted}{initial\ moles\ of\ fructose}\right) \times 100 \quad \text{(A-3)}$$

$$Feed\ Mass\ Ratio = \frac{mass\ of\ fructose}{mass\ of\ DES} \quad \text{(A-4)}$$

$$DES\ Mixing\ Molar\ Ratio = \left(\frac{acid\ moles}{salt\ moles}\right) \quad \text{(A-5)}$$

Appendix B: DES Mixing Molar Ratio Calculations

In this work, the DES was prepared in different molar mixing ratios. Here, the preparation of a 1:1 molar mixing ratio of DES composed of ChCl and p-TSA is given as an example, as illustrated in Table B-1.

Table B-1. DES preparation in 1:1 molar mixing ratio and different fructose mass ratios work sheet

DES preparations 1:1 molar ratio (salt-to-acid)

ChCl molar mass (g/mole)	139.62	ChCl Mass (g)	p-TSA Mass (g)
PTSA molar mass (g/mole)	190.22	139.62	190.22
ChCl Moles	1	1.0	1.362412262
PTSA Moles	1		

	Total DES mass (g)	1.0000	1.3624	2.3624

Feed (Fructose) Mass ratio (w/w)	Total DES mass (g) × ratio (w/w)
2.5	0.0591
5	0.1181
10	0.2362
20	0.4725
30	0.7087
40	0.9450
50	1.1812
60	1.4174
70	1.6537
80	1.8899
90	2.1262
100	2.3624

The molar mass ratio was calculated as moles of acid divided by moles of salt, as shown in Equation (A-5).

Firstly, as illustrated in Table B-1, a mass equivalent to one mole of ChCl and p-TSA was calculated as follows: Choline chloride molar mass = 139.62 g/ mole.

$$Molar\ mass = \frac{mass\ (g)}{number\ of\ moles} \quad \text{(B-1)}$$

Mass of ChCl equivalent to one mole = $\left(139.62\ {}^{g}/_{mole}\right)(1\ mole)$ = 139.62 g of ChCl.

To scale down the used mass of ChCl to 1 g, it was divided by 139.62. The final mass of ChCl weighed on the balance was $\frac{139.62}{139.62}$ = 1 g of ChCl. A similar procedure was carried out for the acid.

p-TSA molar mass = 190.22 g/mole.

Mass of p-TSA equivalent to one mole = $\left(190.22\ {}^{g}/_{mole}\right)(1\ mole)$ = 190.22 g of p-TSA. For a molar mass ratio of 1:1 using 1 g ChCl, the amount in grams of p-TSA required is = $\frac{190.22}{139.62}$ = 1.3624 g of p-TSA.

Appendix C: Initial Mass Ratio of Substrate Fructose Calculations

As shown in Table B-1 above, the substrate fructose was added to the reaction in different feed ratios in order to study the effect of the initial fructose concentrations on the dehydration reactions. In this section, the equivalent mass ratio of 5 is given as an example of the calculation as follows:

$$\text{The total mass of DES} = (total\ mass\ of\ salt) + (total\ mass\ of\ acid) \quad \text{(C-1)}$$

The total mass of DES = $(1g\ of\ ChCl) + (1.3624\ g\ of\ pTSA)$ = 2.3624 g of DES.

For the ratio of 5 of initial fructose mass, Equation (A-4) is used.

Fructose mass = $(feed\ mass\ ratio)(total\ DES\ mass)$ = $(0.05)(2.3624)$ = 0.1181 g of fructose is required for the dehydration reaction.

Appendix D: Experimental Sample Calculations after HPLC Analysis

Following analysis of the sample by HPLC, an area under the curve was obtained for both substrate fructose and the final product 5HMF. The calculation procedure is detailed for a random real experimental sample as an example shown in Table D-1.

From the HPLC analysis, the area under the curve for fructose sample = 105627

Actual fructose mass weighed on the balance prior to the start of the reaction = 0.1182 g

Sample total volume = 100 ml

Fructose molar mass = 180.16 g/mole

Initial fructose moles = $\frac{0.1182\ g}{180.16\ (g/mole)} = 0.000656\ moles\ of\ fructose$

From the fructose calibration curve equation in Figure E-1, Y = 73382 X – 4606.7:

The non-reacted fructose concentration is equal to:

X = $\frac{(105626.5+4606.7)}{(73382)} = 1.50\ mM$

$$Molarity = \frac{number\ of\ moles\ (mole)}{total\ volume\ (litre)} \qquad \text{(D-1)}$$

Number of non-reacted moles of fructose = $(Molarity)(total\ volume)$ =

(1.5 mM /1000×100 ml/1000) = 0.00015 moles of non-reacted fructose.

Reacted moles fructose = $(initial\ fructose\ moles) - (\ non\ reacted\ fructose\ moles)$

= $(0.000656)\ -(0.00015) = 0.000506\ moles$ reacted

From Equation (A-3) above:

Fructose conversion (mol%) = $\frac{0.000506}{0.000656} \times 100 = 77.1$

From the HPLC analysis, the area under the curve for the 5HMF sample = 291315

From the 5HMF calibration curve equation in Figure E-3, Y = 68197 X + 628.68:

The concentration of produced 5HMF is equal to:

X = $\frac{291314.5-628.68}{68197} = 4.26\ mM$

From Equation (D-1) above:

Produced 5HMF moles = $(4.26\ mM/1000)(100\ ml/1000) = 0.0004262\ moles\ of\ 5HMF$

From Equation (A-1) in Appendix A:

5HMF yield (mol%) = $\frac{0.0004262}{0.000656} \times 100 = 64.9$

From Equation (A-2):

5HMF selectivity (mol%) = $\frac{0.0004262}{0.000506} \times 100 = 84.2$

Table D-1: Analysed sample data sheet

Experiment No.	**R. Temp. 50 °C 29 01 2014**		
Fructose mass (g)	**0.1182**	**Fructose in moles**	**0.0006561**
Fructose MW (g/mole	**180.16**	**non reacted Fructose Concentration (mM)**	**1.5021831**
Fructose Calib. Values	********	**non reacted Fructose moles**	**0.0001502**
A	**73382**	**Reacted Fructose moles**	**0.0005059**
B	**4606.7**		
Fructose Area	**105627**	**5HMF produced moles**	**0.0004262**
Total Volume (ml)	**100**	**5HMF produced Concentration (mM)**	**4.2624429**
5HMF Calib. Values	********		
C	**68197**		
D	**628.68**	**Fructose Conversion %**	**77.1037812**
5HMF Area	**291315**	**5HMF Yield %**	**64.9679964**
		5HMF Selectivity %	**84.2604544**
Fructose Mass (%)	**5**		
ChCl mass (g)	**1.0004**		
PTSA mass (g)	**1.3626**		
Reaction Temp. °C	**50**		
Reaction time (min)	**60**		
Volume of water added (ml)	**10**		
DES Mixing molar ratio	**1 to 1**		
DES Mixture heating time 10 minutes			
Fructose Retention Time (min)	**16.724**		
HMF Retention Time (min)	**35.021**		
pH Initial	**0.449**		
pH Final	**7.075**		

Appendix E: Calibration Curves Calculations

Initially, calibration curves for the fructose and 5HMF were generated in a concentration range from 15 to 1.5 mM. The calculations were performed as follows:

Appendix E-1: Fructose Calibration Curve Calculations

Firstly, 15 mM stock solution of fructose was prepared using HPLC grade water in a total volume of 10 ml.

Fructose molar mass = 180.16 g / mole

Total volume = (10 ml) / (1000) = 0.01 litre

15 mM= (15 mM)/1000 = 0.015 M

From Equation (D-1) above:

Number of moles = (0.015 M) × (0.01litre) = 0.00015 moles

Mass of fructose required to form 15 mM stock solution is equal to (180.16 g⁄mole) (0.00015 moles) = 0.027 g.

Therefore, 0.027 g of fructose was weighed on the balance and dissolved in 10 ml of HPLC grade water, then 1 ml of this stock solution was poured in a 2 ml HPLC vial.

For the lower concentration sample calculation (12 mM), Equation (E-1) was used:

$$C_1.V_1 = C_2.V_2 \quad \text{(E-1)}$$

Where:

C_1: the stock solution concentration, which is 15 mM;

V_1: the volume required to be taken from the stock solution to form a new concentration sample of 12 mM;

C_2: the target concentration, which is 12 mM;

V_2: target volume of the new sample, which is 1 ml.

Therefore, and according to Equation (E-1), the required volume to be taken from the stock solution is V_1 (ml) = $\frac{(C_1)(V_2)}{C_1}$ = $\frac{(12mM)(1ml)}{(15mM)}$ = 0.8 ml.

So, to form a 1 ml sample of 12 mM concentration, 0.8 ml of stock solution was taken by pipette and poured in a 2 ml clean HPLC vial, then 0.2 ml of the HPLC grade water was added to the vial and shaken well. The same procedure was carried out for the preparation of the rest of the samples. The calibration curve is plotted as shown in Figure E-1.

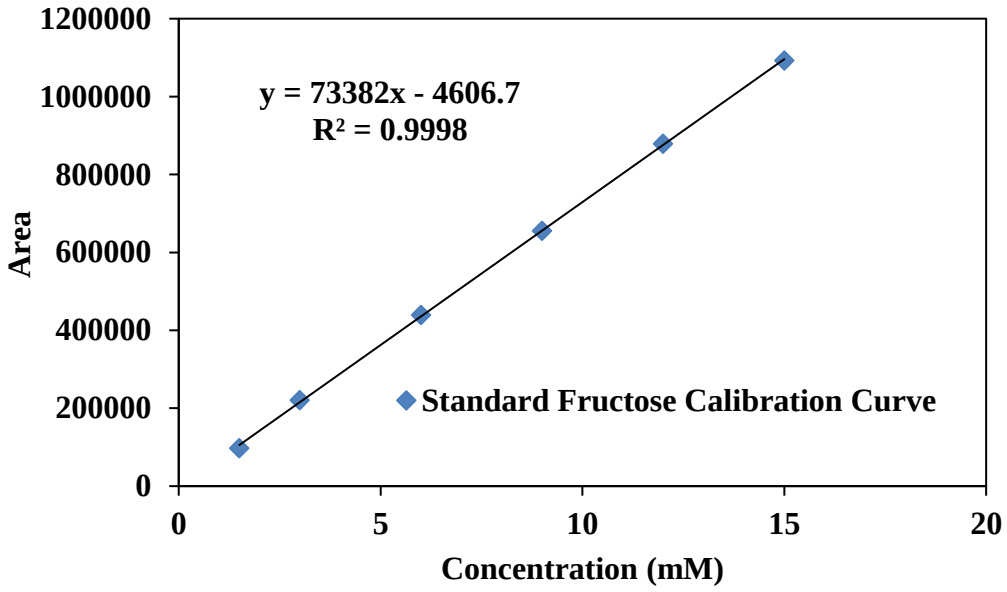

Figure E-1: Fructose calibration curve

Later, the ranges of calibration curve of fructose were extended from 0.0375 to 15 mM, as illustrated in Figure E-2.

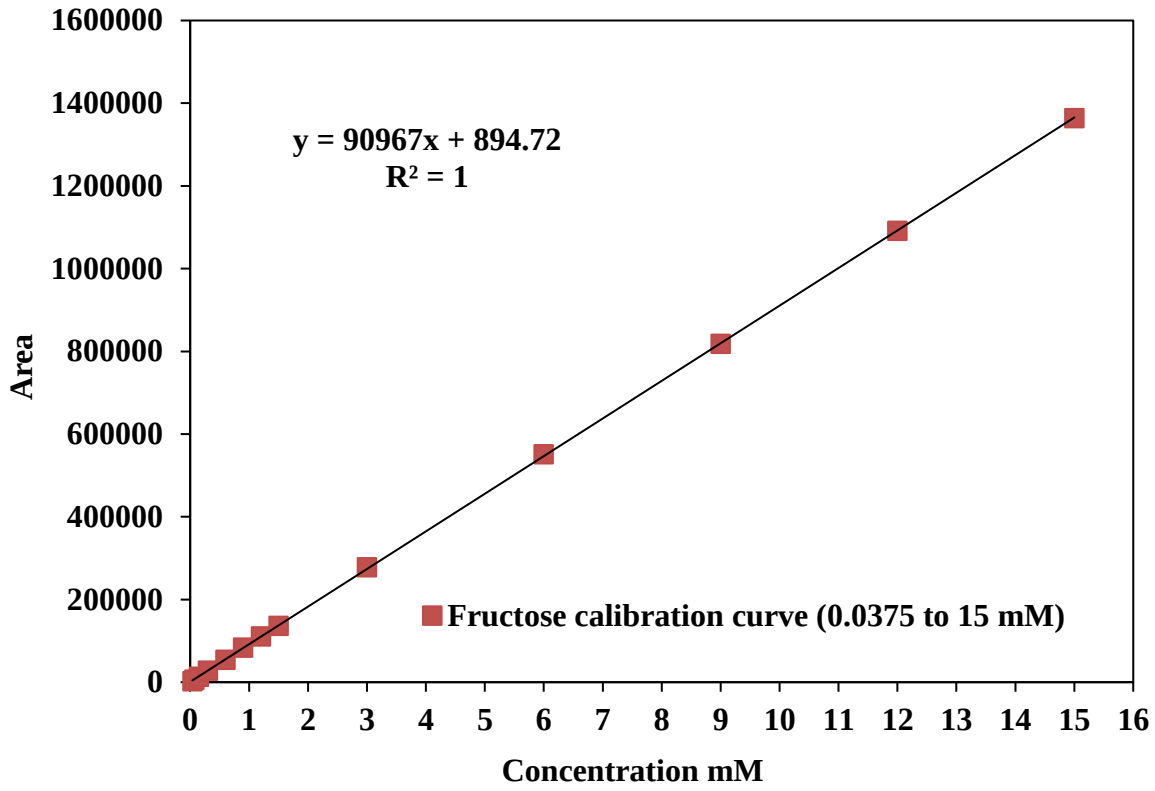

Figure E-2: Extended calibration curve of fructose

Appendix E-2: 5HMF

10 ml (0.01 litre) of 15 mM (0.015 M) 5HMF stock solution was prepared. 5HMF molar mass = 126.11g / mole.

Similarly to the procedure carried out above, the number of 5HMF moles are equal to $(Molarity)(total\ volume) = \left(0.015\ {}^{mole}/_{litre}\right)(0.01\ litre) = 0.00015$ mole, while the required mass of 5HMF to form 15 mM stock solution is equal to $(5HMF\ molar\ mass)(5HMF\ moles) = \left(126.11\ {}^{g}/_{lmole}\right)(0.00015\ mole) = 0.0190$ g of 5HMF. The lower concentrations are calculated in a similar procedure mentioned above. The calibration curve of 5HMF is plotted as shown in Figure E-3.

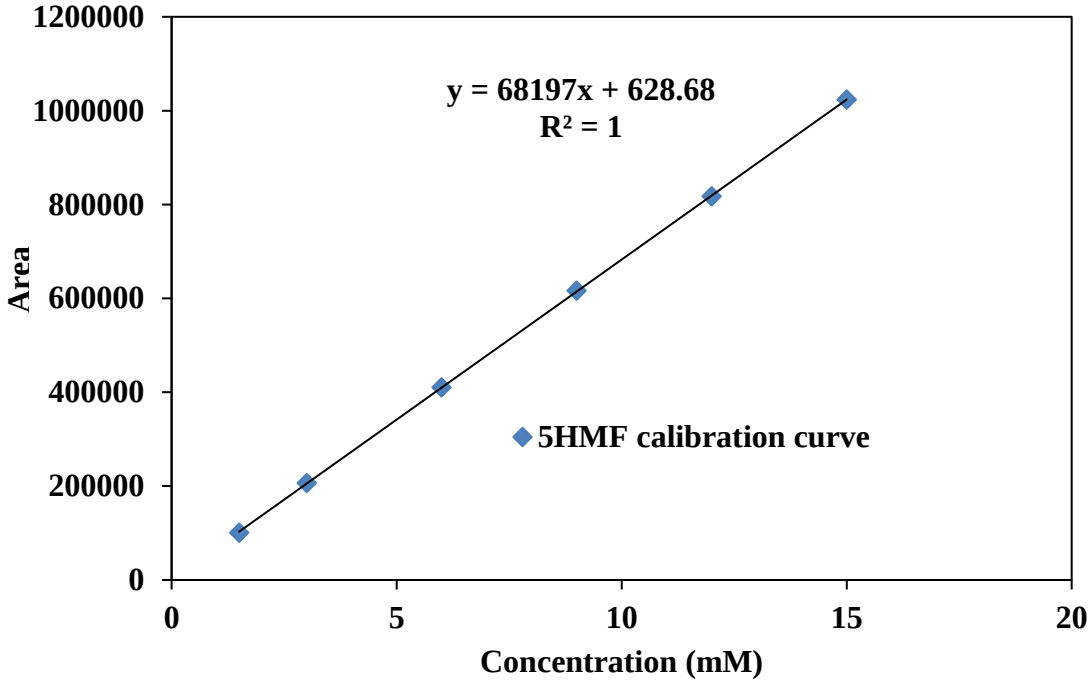

Figure E-3: 5HMF calibration curve

The calibration curve range was extended from 0.002 to 30 mM, as shown in Figure E-4.

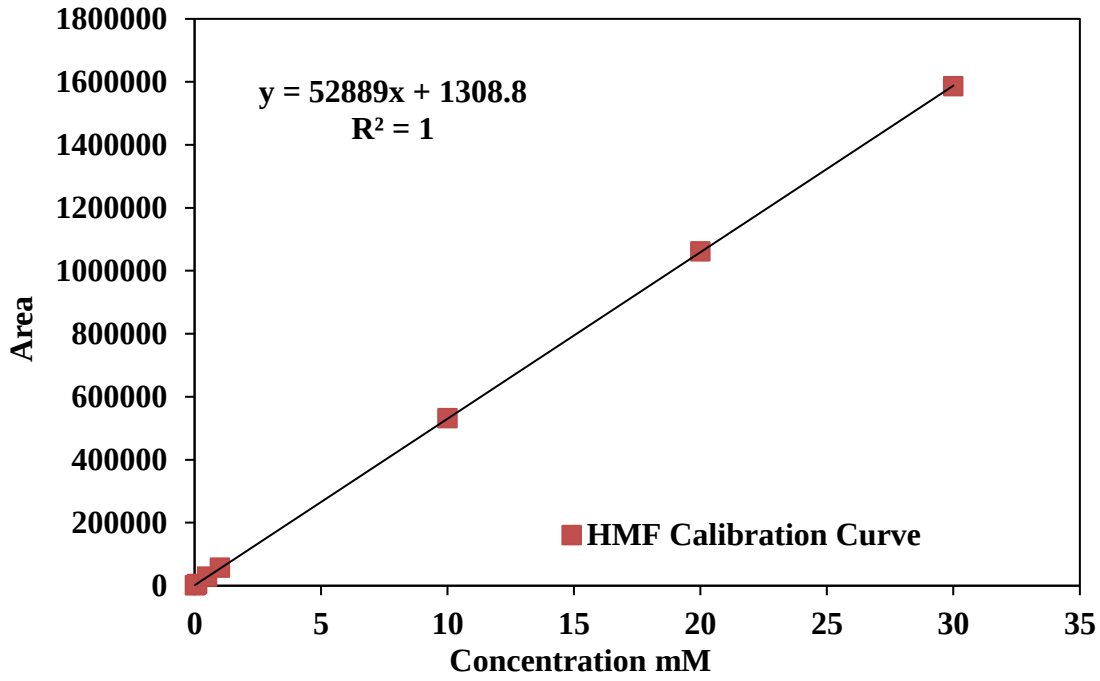

Figure E-4: Extended calibration curve of 5HMF